Engineering the Optical Properties of Luminescent Solar Concentrators at the Molecular Scale

by

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B.Sc., Delft University of Technology (2005)
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Submitted to the Department of Electrical Engineering and Computer Science

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Abstract

Luminescent Solar Concentrators (LSCs) concentrate solar radiation onto photovoltaic (PV) cells using an inexpensive collector plate to absorb incoming photons and waveguide fluorescently re-emitted photons to PVs at the edge. This thesis addresses the two main energy loss mechanisms in LSCs, namely transport losses and trapping losses.

We used phycobilisomes, a biological light-harvesting complex, as dyes in the LSC collector to circumvent transport losses caused by photon re-absorption. The self-assembled structure of phycobilisomes couples numerous donor chromophores to a handful of acceptor chromophores through an internal Förster energy pathway that isolates the absorption and emission spectra. We established that energy transfer within intact phycobilisomes reduces LSC self-absorption losses by approximately \((48\pm5)\%\) by comparing intact and partly decoupled phycobilisome complexes.

To reduce trapping losses in LSCs, we leveraged the anisotropic emission pattern of dichroic dye molecules. We aligned their dipole moments normal to the face of the waveguide by embedding them in a liquid crystal host. Vertical dye alignment increased the fraction of the power emitted below the critical angle of the waveguide, thereby raising the trapping efficiency to 81% from 66% for LSCs with unaligned dyes. The enhanced trapping efficiency was preserved for geometric gains up to 30, and an external diffuser can enhance absorption in LSCs with vertically-aligned dyes.

This thesis also explores an energy harvesting strategy for portable electronics based on LSCs with dye molecules that are aligned in-plane. The purely absorptive polarizers used to enhance contrast ratios in displays can be replaced with two linearly polarized luminescent concentrators (LSCs) that channel the energy of absorbed photons to PVs at the edge of the display. We coupled up to 40% of incoming photons to the edge of a prototype LSC that also achieved a polarization selection ratio of 3.

Finally, we investigated the contribution of self-absorption and optical waveguiding to triplet exciton transport in crystalline tetracene (Tc) and rubrene (Rb). A time-resolved imaging technique that maps the triplet distribution showed that optical
waveguiding dominates over diffusion and can transport energy several micrometers at the high excitation rates commonly used to probe the exciton diffusion constants in organic materials.

Thesis Supervisor: Marc A. Baldo
Title: Associate Professor
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## Contents

1 **Introduction and Motivation**  
1.1 The need for cheaper solar energy  
1.2 Solar Concentrators  
1.2.1 Geometric Solar Concentrators  
1.2.2 Competitiveness of geometric solar concentrators  
1.3 Luminescent Solar Concentrators (LSCs)  
1.3.1 The operating principle of LSCs  
1.3.2 The advantages of Luminescent Solar Concentrators  
1.3.3 State-of-the-art LSCs  
1.3.4 The economics of LSCs  
1.3.5 The thermodynamic limit to the concentration potential of LSCs  
1.3.6 The operational losses of LSCs  
1.3.7 Engineering the optical properties of LSCs at the molecular scale  
1.4 Thesis roadmap  

2 **Luminescent Solar Concentrators Employing Phycobilisomes**  
2.1 Introduction  
2.1.1 Förster Energy Transfer  
2.1.2 Reducing self-absorption using Förster energy transfer  
2.2 Phycobilisomes  
2.3 Experimental Section  
2.3.1 Phycobilisome preparation  
2.3.2 Solid-state phycobilisome waveguide  
2.3.3 Transport losses and Förster energy transfer  
2.4 Conclusions  

3 **Dye Alignment in Luminescent Solar Concentrators: I. Vertical Alignment for Improved Waveguide Coupling**  
3.1 Introduction  
3.1.1 The Origin of trapping losses in LSCs  
3.1.2 Increasing the trapping efficiency by aligning dichroic dyes  
3.1.3 Chapter Outline  
3.2 Trapping Efficiency - Theoretical Predictions  
3.3 Device Fabrication  
3.3.1 Vertically aligned LSC fabrication  

15  
15  
16  
18  
22  
23  
23  
24  
25  
27  
28  
30  
32  
32  
35  
35  
36  
38  
39  
42  
42  
44  
47  
50  
53  
53  
54  
55  
57  
60  
61
3.3.2 Isotropic LSC fabrication
3.4 Experimental Techniques
3.4.1 Measuring the trapping efficiency
3.4.2 Measuring the angular dependence of the absorption
3.4.3 Measuring the performance versus optical concentration
3.4.4 Monte Carlo ray tracing model
3.5 Experimental Results
3.5.1 Measured trapping efficiency
3.5.2 Absorption as a function of the incident angle
3.5.3 The performance versus optical concentration
3.6 Discussion and Conclusions

4 Dye Alignment in Luminescent Solar Concentrators: II. Horizontal Alignment for Energy Harvesting in Displays
4.1 Motivation for energy harvesting in displays
4.2 Strategy and device layout
4.3 Linearly Polarized LSC Fabrication
4.4 Experimental LP-LSC Device Characterization
4.4.1 Absorption and photoluminescence
4.4.2 The optical quantum efficiency spectra
4.4.3 The external quantum efficiency versus optical concentration
4.5 Extending the absorption of LP-LSCs over the full visible spectrum
4.6 Conclusions and Outlook

5 The Contribution of Waveguiding and Self-absorption to the Transport of Triplet Excitons in Tetracene and Rubrene Crystals
5.1 Introduction
5.2 Experimental methods
5.3 Experimental results
5.4 Simulations
5.5 Discussion and Conclusion

6 Conclusions and Outlook

A Saturated And Efficient Blue Phosphorescent Organic Light Emitting Devices With Lambertian Angular Emission
A.1 Introduction
A.2 Device Structure and Fabrication
A.3 Optical cavity design
A.4 Experimental characterization
A.4.1 OLED Quantum Efficiency
A.4.2 Transmission of Scattering filters
A.4.3 Angular Dependence EL Spectra
A.5 Conclusions
## List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>The growing competitiveness of solar power</td>
<td>16</td>
</tr>
<tr>
<td>1-2</td>
<td>Two examples of traditional solar concentrators</td>
<td>18</td>
</tr>
<tr>
<td>1-3</td>
<td>The acceptance angle of a geometric concentrator</td>
<td>19</td>
</tr>
<tr>
<td>1-4</td>
<td>The maximum concentration of a passive concentrator</td>
<td>20</td>
</tr>
<tr>
<td>1-5</td>
<td>Electricity costs generated with a CPV system</td>
<td>21</td>
</tr>
<tr>
<td>1-6</td>
<td>Schematic and picture of a luminescent solar concentrator</td>
<td>23</td>
</tr>
<tr>
<td>1-7</td>
<td>The monochromaticity of the light concentrated at the edges of an LSC</td>
<td>25</td>
</tr>
<tr>
<td>1-8</td>
<td>The Stokes shift</td>
<td>29</td>
</tr>
<tr>
<td>1-9</td>
<td>Illustration of the compounding effect of self-absorption</td>
<td>32</td>
</tr>
<tr>
<td>2-1</td>
<td>The process of Förster energy transfer</td>
<td>37</td>
</tr>
<tr>
<td>2-2</td>
<td>Antennas in photosynthesis</td>
<td>39</td>
</tr>
<tr>
<td>2-3</td>
<td>A schematic representation of the structure of a phycobilisome</td>
<td>40</td>
</tr>
<tr>
<td>2-4</td>
<td>The PL spectra of the three types of phycobiliproteins used in this study.</td>
<td>41</td>
</tr>
<tr>
<td>2-5</td>
<td>Chromic adaptation of phycobilisomes</td>
<td>41</td>
</tr>
<tr>
<td>2-6</td>
<td>Incorporation of intact phycobilisomes in a solid state matrix</td>
<td>44</td>
</tr>
<tr>
<td>2-7</td>
<td>Optical Quantum Efficiency of a solid state PBS film</td>
<td>46</td>
</tr>
<tr>
<td>2-8</td>
<td>Schematic and picture of the EQE set-up of liquid based PBS-LSCs</td>
<td>49</td>
</tr>
<tr>
<td>2-9</td>
<td>The absorption and emission spectra of the phycobilisome complexes employed in the water-based LSCs and their EQE</td>
<td>52</td>
</tr>
<tr>
<td>3-1</td>
<td>Dichroic dye molecules are used to increase the trapping efficiency of an LSC</td>
<td>55</td>
</tr>
<tr>
<td>3-2</td>
<td>A polymerizable liquid crystal host is used to align the dyes with respect to the waveguide</td>
<td>56</td>
</tr>
<tr>
<td>3-3</td>
<td>Schematic representation of the dipole orientation within the waveguide of the LSC</td>
<td>58</td>
</tr>
<tr>
<td>3-4</td>
<td>The calculated trapping efficiency as a function of the dipole orientation and refractive index</td>
<td>59</td>
</tr>
<tr>
<td>3-5</td>
<td>The calculated trapping efficiency of an LSC as a function of the angle of the incident light</td>
<td>60</td>
</tr>
<tr>
<td>3-6</td>
<td>A schematic representation of the measurement set up used to determine the trapping efficiency and angular dependence of the absorption of an LSC</td>
<td>63</td>
</tr>
<tr>
<td>3-7</td>
<td>The measured trapping efficiency</td>
<td>67</td>
</tr>
</tbody>
</table>
A-5  The color coordinates of the strong microcavity devices with and without holographic diffusers and a photograph of a pixel . . . . . . . . . 117
A-6  The angular emission profile of the strong microcavity Flrpic OLED as a function of angle and SEM images of the holographic diffuser . . 118
Chapter 1

Introduction and Motivation

1.1 The need for cheaper solar energy

The cost of solar power decreases every year, and is reaching grid parity in certain parts of the world. Nevertheless, the world needs to see major cost reductions before major economies will opt for this clean source of energy. Figure 1-1 illustrates the economics underlying this fact. The average prices of electricity per household in major economies of the world are plotted against the annual solar energy yield in those countries. The position on the x-axis indicates how much sunlight each country receives, with countries to the right having greater access to solar energy. The position on the y-axis indicates the current cost of electricity from the grid in each country, which is the cost with which solar energy needs to compete. The size of the orange symbols reflects the size of the electricity market in each country. In 2008, the countries situated in the dark green area in the upper right of Figure 1-1 reached grid parity for solar energy, and countries in the light green area are projected to reach grid parity in 2020. Nevertheless, we need to significantly reduce the cost of solar electricity for it to replace non-renewable and clearly harmful forms of energy generation like coal power plants in major economies in the world, especially China.
Figure 1-1: The motivation for price reduction in solar energy generation. In order for major economies like China and India to switch to clear solar energy we need to significantly reduce its price. Figure taken from [1].

and India.

1.2 Solar Concentrators

Solar energy is expensive mainly because photovoltaic (PV) elements are expensive. An old strategy to reduce the PV cost is to use a solar concentrator. The idea is to gather light using a large, inexpensive collector and concentrate it onto a small PV element. The geometric concentration factor is called $G$, and is defined as the ratio of the area of the collector to the area of the PV element:

$$G = \frac{A_{\text{collector}}}{A_{\text{PV}}}$$  (1.1)

The real figure of merit for reducing the cost of a PV concentrator system is the flux gain, $F$, which is equal to the geometric gain corrected for efficiency losses in the
where \( \eta_{EQE} \) is the external efficiency of the concentrator. The following economic equation describes how the price (in dollars per Watt-peak, \( W_p \)) of generating solar energy scales with the properties of a solar concentrator system:

\[
\frac{\text{\$/W}_p}{\text{efficiency} \times \text{solar flux}} = \frac{1}{F \text{efficiency} \times \text{solar flux}} + \text{Maintenance} \tag{1.3}
\]

As \( F \) increases, the cost of the shrinking PV eventually becomes negligible relative to the entire system, which is driven by the cheap collector. Thus, to reduce the cost of solar energy, the flux gain, \( F \), needs to be large and the collector cost low, while keeping maintenance costs at a minimum.

Another advantage of a solar concentrator system is that the efficiency of the PV element becomes enhanced under high illumination. This enhancement is the result of the linear increase in the short circuit current of the PV, \( I_{SC} \), with concentration factor \( F \), and the logarithmic increase in the open circuit voltage, \( V_{OC} \), with \( I_{SC} \) \cite{2};

\[ V_{OC} \approx \frac{k_B T}{q} \ln \frac{I_{SC}}{I_0}. \]

The \( F \) dependent efficiency of a PV element, \( \eta^{F\text{sun}} \), is then given by \cite{2}:

\[
\eta^{F\text{sun}} = \eta^{1\text{sun}} \left( \frac{FF^{F\text{sun}}}{FF^{1\text{sun}}} \right) \left( \frac{1 + \frac{k_B T}{q} \ln F}{V_{OC}^{1\text{sun}}} \right). \tag{1.4}
\]

In Equation 1.4, \( \eta^{1\text{sun}} \) is the PV efficiency under 1 sun illumination (1000 W/m\(^2\)); \( FF^{1\text{sun}} \) and \( FF^{F\text{sun}} \) are the (somewhat confusingly, though conventionally named) fill factors of the PV element under 1 sun and \( F \) suns of illumination, respectively; \( k_B \) is Boltzmann’s constant; \( T \) is the temperature; \( q \) is the elementary charge; \( V_{OC}^{1\text{sun}} \) is the open circuit voltage at 1 sun illumination. We note that Equation 1.4 only holds under the assumptions that the PV semiconductor parameters (e.g. the bandgap, refractive index, extinction coefficient, mobility, etc.) do not change under the increased illumination, and that the temperature remains constant.
1.2.1 Geometric Solar Concentrators

Figure 1-2: Two examples of conventional concentrator systems: (a) Fresnel lens and (b) a mirror based concentrator. Both systems are capable of achieving high concentration factors, but in order to do so, they must track the sun. Also, the PV elements need to be cooled, and these systems only work under clear sky conditions. Both pictures are taken from [3].

Figure 1-2 presents two examples of traditional solar concentrators systems: (a) one based on Fresnel lenses and (b) a mirror-based concentrator. These systems are known as "geometrical" or "passive" concentrators, because the photons passing through such optical systems are unchanged in energy.

Winston was the first to derive an expression for the maximum concentration factor obtainable for a geometric concentrator [4]. For a Lambertian light source at infinity (a good approximation for the Sun), the maximum optical concentration depends on the incident angle of light relative to the normal of the optical collector, $\theta_I$ (see Figure 1-3), as follows [5]:

$$G_{\text{max}} \leq \frac{1}{\sin^2 \theta_I}$$  \hspace{1cm} (1.5)
Figure 1-3: The maximum concentration factor obtainable with a passive, geometric concentrator depends on the angle of that the incident light makes with the normal, $\theta_I$. The acceptance angle is the maximum angle at which incoming sunlight can be captured by a solar concentrator.

For a geometric concentrator made of a medium with refractive index $n$, which also surrounds the exit plane of the concentrator, the maximum concentration is given by:

$$G_{\text{max}}(n) \leq \frac{n^2}{\sin^2 \theta_I}$$

Equations 1.5 and 1.6 are also known as the sine brightness equations. They are based on the conservation of optical flux and radiance through the geometric optical system. The same expressions can also be derived from the second law of thermodynamics by considering the transfer of heat radiation (see, for instance, the derivations by Rabl [6] or Chaves [7]).

Figure 1-4 plots the maximum concentration as a function of $\theta_I$. High concentration factors ($> 1000$) can only be achieved if $\theta_I$ is smaller than $\sim 1^\circ$, hence, the orientation of geometric concentrators must track the sun. The very high influx of sunlight also causes the temperature of the PV to rise, because photons with energies greater than the bandgap energy, $E_G$, need to thermalize to the bandgap edge after absorption. This effect is know to degrade the performance of silicon solar cells ($E_G$
Figure 1-4: The maximum concentration factor of a passive, geometric concentrator as a function of the angle of the incident light, $\theta_I$ follows a $1/\sin \theta_I^2$ behavior. To obtain concentrations above $G = 1000$ the system must track the sun.

= 1.1 eV) by 0.45 % per degree Celsius, whereas wider-bandgap GaAs cells (1.4 eV) lose about 0.21% per degree Celsius [8]. Furthermore, ohmic losses within the solar cell result from the large currents flowing through it at high $G$. Ohmic losses, which are proportional to $I^2R_S$, where $R_S$ is the series resistance [9], require the solar cells to be actively cooled. Tracking and cooling requirements increase the maintenance and capital costs for geometric concentrators, while further complicating module and cell design. Moreover, the entire concentrator system wastes valuable real estate around its perimeter to avoid shadowing neighboring concentrators, again adding to the maintenance costs in Eq. 1.3.

Finally, geometric concentrator systems are only capable of collecting sunlight effectively under clear sky conditions, because it becomes impossible to create a good image of the sun on the PV if clouds scatter the light in all directions. The maximum concentration under diffuse radiation is limited to $G = n^2$, where $n$ is the refractive index of the collector [5, 6].
Figure 1-5: The calculated cost of electricity generated by a solar concentrator system operating at 3 different concentration factors: 100, 500 and 1000 suns. The calculation has been performed for 4 different cell efficiencies, ranging from 22% to 28%, and 5 different solar cell cost estimates for the solar cells employed in the system ranging from very low (Euro 2 cm$^{-2}$; the possible result of strong innovation), low, medium, high, to very high cost (Euro 20 cm$^{-2}$, occurring in the case of stressed market or scarcity). These calculations are representative for Madrid. The reference level for the competitiveness of the cost of CPV electricity is taken to be 0.1 Euro/kWh. From [10].
1.2.2 Competitiveness of geometric solar concentrators

The cost of generating electricity with a geometric concentrator system depends on a few key parameters (see Eq. 1.3). Figure 1-5 presents the cost of electricity generated by a concentrated PV (CPV) system in Madrid, as calculated by by Algora [10], and compares it to the target price of 0.1 Euro/kWh (which would lead to wide-spread adaptation of CPV at the local utility scale). Algora considered CPV systems for different costs of the PV element, the efficiency of the PV, and the concentration factor of the optics. The current price for high-performance (III–V compound semiconductors like GaAs) solar cells is \( \sim \) Euro 6-8 cm\(^{-2}\) [11], but Fig. 1-5 also presents scenario’s where the price is lower or higher (representing PV-market situations of strong innovation in PV and scarcity, respectively). As can be observed, for the scenario’s in which the solar cells costs are relatively low (2 and 6 Euro/cm\(^2\)), the influence of the concentration factor on the electricity cost is relatively low compared to the high PV cost scenarios (10 and 20 Euro/cm\(^2\)).

At present, the geometric solar concentrator PV strategy is cost effective, but only under certain conditions. Commercial systems are currently being deployed in desert locations in Arizona, California and Spain, where unobscured sunlight is plentiful, and where large areas are available to help minimize the operation and maintenance cost through economies of scale. An example of a commercial CPV product is the parabolic mirror concentrator system from SolFocus. Their ground-mounted system operates at \( 650 \times \) concentration factor, and employs a III-V cell (gallium arsenide (GaAs) on germanium (Ge) substrates with a \( \sim 40\% \) efficiency) that is passively cooled [12].
Figure 1-6: (a) A schematic representation of a luminescent solar concentrator (LSC). Solar radiation is absorbed by highly fluorescent dye molecules integrated in a thin, flat-plate waveguide. The dye re-emits photons at a lower energy, which can then be guided to solar cells attached to the edge of the plate by total internal reflection. This is where solar cells can be placed which collect the photons and convert them into electricity. For a conventional LSC employing isotropically aligned dye molecules, approximately 75% of the radiation is trapped in the waveguide. (b) A picture of a LSC. Notice the brightness of the edges.

1.3 Luminescent Solar Concentrators (LSCs)

The challenges faced by geometric solar concentrators motivated the invention and investigation of a different concept, Luminescent Solar Concentrators (LSCs).

1.3.1 The operating principle of LSCs

Invented in 1976 by Weber and Lambe [13], LSCs aim to reduce the cost of solar electricity by using an inexpensive collector to concentrate solar radiation without mechanical tracking [13, 14, 15, 16, 17, 18, 19, 20]. A luminescent solar concentrator is a conceptually simple structure illustrated in Figure 1-6; a luminescent dye is embedded in a planar waveguide made of any optically clear material with a refractive index larger than 1. Incoming solar radiation is absorbed by the fluorescent dye at an energy $\epsilon_1$, which then re-emits a photon at a lower energy, $\epsilon_2$, through photo-
luminescence. Photons re-emitted at sufficiently glancing angles to the waveguide surface, below the critical angle $\theta_C$ for total internal reflection, become trapped in the waveguide and are transported to its edge. A solar cell is attached to the edge of the waveguide to absorb the photons and convert their energy into electricity.

Since the area of the face of the waveguide exceeds the area of the edge, light can become concentrated. The geometric concentration factor of an LSC is the area of the face divided by the area of the PV element. For a square LSC with PV elements covering the 4 edges, $G = L/4d$, where $L$ is the length of a side and $d$ is the thickness of the plate. In this way, the LSC strategy allows light to be collected and concentrated using a cheap, flat plate (see Fig. 1-6(b)), thereby allowing the size of the expensive PV element to be greatly reduced.

### 1.3.2 The advantages of Luminescent Solar Concentrators

LSC technology offers several important advantages over the conventional, geometric concentrators discussed in Section 1.2.

1. The fabrication of the concentrator is compatible with low cost manufacturing processes such as molding, coating and casting. Their primary structure is relatively simple in that it is based on nothing more an optically clear waveguide, a dye, and packaging. The LSC concept does not require scarce materials such as indium, tellurium or gallium [21].

2. LSCs do not need to track the sun to obtain high concentration factors, thanks to the isotropic absorption of the dyes in the plate; consequently, LSCs can concentrate both direct and diffuse sunlight. This property significantly reduces the complexity and the cost of the concentrator system.

3. The solar cells do not require cooling because their bandgap can be perfectly matched to the nearly monochromatic light emitted by the dye molecules (see
Figure 1-7: The monochromaticity of the light concentrated at the edge of an LSC allows for a perfect tuning of the PV bandgap to this energy, reducing thermalization losses within the PV element. Picture taken in the Baldo lab.

Figure 1-7), ensuring that the entire photon energy is collected and not dissipated as heat.

4. LSC are architecturally interesting. They are naturally suited for integration into windows, because their transparency can be easily tuned and the PV element can be embedded in the window frame.

5. LSC systems are inherently tolerant of defects in fabrication and are relatively insensitive to shadowing by dirt or leaves. Uneven illumination is not a problem because the isotropic emission by dye molecules ensures the concentrated light is evenly distributed over the PV.

6. LSCs can be placed in close proximity to each other without risk of shadowing neighbors from the sun.

1.3.3 State-of-the-art LSCs

Materials: A typical LSC design consists of a polymeric plate, such as Poly(methylmethacrylate) (PMMA), acrylic or polycarbonate, that is doped at a low concentration with a fluorescent organic dye. Popular dyes are perylenes [22], a family that has
high PL efficiencies. Furthermore, they have been shown to be stable in a PMMA when a UV absorber is incorporated in the LSC design, which extends the lifetime from a few of months to several years [23]. Quantum dots are another interesting family of dyes for LSC applications [24, 25] because they have a broad absorption spectrum and high absorption coefficients. Furthermore, their emission spectra can be tuned to the near-infra-red, which permits a larger fraction of the solar spectrum to be absorbed and efficiently coupled to the bandgap of silicon solar cells. Finally, their inorganic, crystalline nature is argued to be more stable than organic dyes. Currently, the PL efficiency of commercial dots in a solid state film is too low, ~10%-45% [26], to be relevant for LSC technology. Especially considering the high costs of high quality material, with a current average cost of quantum dots running from $2500 and $6000 per gram [27], which compares negatively to cost estimates for fluorescent organic dyes at roughly $500/gram [11]).

Glass substrates doped with rare earth (RE) materials like Nd$^{3+}$ or Yb$^{3+}$ are another interesting approach. REs have high photo-stability, and can have very high PL efficiencies [17]. Unfortunately, their absorption spectra are very narrow and overlap poorly with the solar spectrum, necessitating an additional sensitizer material to utilize the full solar spectrum [17].

Currie et al. introduced a strategy employing a thin film (\(\sim 1 \mu\text{m}\)) of organic dye molecules on a transparent substrate [19]; the organic solar concentrator (OSC). If the refractive indices of the coating and the substrate are matched, the re-emitted light is guided by both the substrate and the thin film. The appeal of this approach will be further discussed in Chapter 2.

Finally, Rogers et al. recently reported on a luminescent concentrator system that employs an array of surface-embedded, "\(\mu\)-silicon solar cells that have micrometer-sized dimensions. These small dimensions and the overall design of their \(\mu\)-cells allow capture of light not only through their top surfaces, but also through their sidewalls
and bottom surfaces. Their LSC design can employ ultra-thin (tens of μm) and mechanically flexible substrates [28].

**Performance:** LSCs were extensively studied in the late 1970s and in the 1980s. In 1984, Wittwer et al. reported a total power conversion efficiency of 4% for a LSC stack consisting of two plates with dimensions 40 × 40 × 0.3 cm \((G = 33)\) that were coupled to a GaAs and a Si PV cell, respectively [16]. It was the poor performance of the luminescent dyes that hindered further development of LSCs [29], and few improvements followed for the next 2 decades.

Recent years have witnessed rapid improvements in dye efficiency, cost, and stability thanks to developments in the organic light emitting diode industry, and to the availability of new classes of luminescent species like quantum dots and rare earth materials. Consequently, there has been renewed interest in LSC technology. In 2008, Currie et al. [19] controlled the intermolecular packing of a multi-dye coating on an index matched glass substrate to reduce self-absorption losses in LSCs. They reported calculated power conversion efficiencies of 5.9% for single plate LSCs and 6.8 % for a tandem LSC stack coupled to GaInP and GaAs PV cells. Slooff et al. [18] reported a record power efficiency of 7.1% in 2008 using a LSC consisting of 2 different dyes dispersed in a PMMA matrix, coupled to 4 GaAs cells at the edges. It is difficult to compare the results obtained by different groups directly, however, because LSC efficiencies depend strongly on the geometric gain and on the types of solar cells used.

### 1.3.4 The economics of LSCs

LSCs are not commercially available as of yet, since the flux gains that have been experimentally demonstrated are too low to off-set the high price of the high-performance cells. In his PhD thesis, Jonathan Mapel discusses the cost and efficiency requirements for a successful LSC commercialization in detail [11]. He assumed that in order to compete with conventional power generation, the cost of generating electricity with
a PV system needs be lower than $1/W_p$. Current LSCs employ dye molecules that emit light in the visible range (i.e. below $\lambda = 700$ nm), and are therefore best coupled to GaInP cells ($E_g = 1.81$ eV or $\lambda = 680$ nm). Since GaInP cells are not produced in large quantities, Mapel used the cost model for Emcore’s more complex triple junction solar cells as an approximation. Those cells cost approximately $8/cm^2$ for 0.1 MW$_p$ of capacity. Those devices are 37% efficient, resulting in a net cost of $218/W_p$. Accordingly, if we restrict the cost of the cells to 30% of the total module cost, the flux gain must exceed 700 to be commercially interesting. This flux gain greatly exceeds what is currently available [19, 18].

Instead of using high-performance III-V type PV elements, one could opt for silicon cells. This choice is expected to reduce the cost of a LSC system significantly, since the current price of high performance (mono-crystalline) silicon cells is $1.28/W_p$ at the module level in October 2011 [30]. At cell level the price is expected to be even lower. This reduction in price will come at the cost of a lower power conversion efficiency for the LSC system. The low $V_{oc}$ for Sunpower cells, an example of a mono-crystalline silicon solar cell technology ($V_{oc} = 0.678$ V [31]), relative to GaInP or GaAs cells (1.34 V [32] and 1.05V [2], respectively) is an especially large source of loss. Extending the absorption and emission spectra of the luminescent species towards the silicon bandgap will mitigate this loss in energy.

### 1.3.5 The thermodynamic limit to the concentration potential of LSCs

A good reason for continued interest in LSCs is the tremendous room for innovation that exists. Well-known arguments indicate that the LSC concept has the potential to achieve extremely high geometric concentration factors. We must estimate the maximum $G$ achievable on thermodynamic grounds, rather than the radiance conservation principles used to derive equation 1.5, because the physics underlying LSCs
Figure 1-8: Stokes shift is the distance (in wavelength or in energy) between positions of the peak absorption and peak emission of an electronic transition from the same atom or molecule. It is the result of a lowering of the energy after absorption and before emission due to the relaxation of the excitation to the lowest vibronic state, which typically occurs within a couple of picoseconds [33].

differs crucially from geometric concentrators that we discussed in Section 1.2. We can liken the operation of luminescent solar concentrators to an optical heat pump; light is absorbed at one energy level, $\epsilon_1$, and re-emitted at a lower energy level, $\epsilon_2$, while dissipating the small difference as heat (illustrated in Figure 1-8). Since the absorption and re-emission process does not conserve the photon energy, the radiance and flux need not be conserved, as was the case for geometric concentrators. Relaxing these constraints in fact allows the concentration factor to be increased far beyond the limit for geometric solar concentrators expressed in equations 1.5 and 1.6.

Yablonovitch considered the entropy of the photons in an LSC and of the heat released with fluorescence, and imposed the second law of thermodynamics (requiring the change in entropy to be positive) to derive the following expression for the maximum concentration factor of an LSC employing a dye system absorbing photons at energy $\epsilon_1$ and re-emitting them at energy $\epsilon_2$[34, 5]:

$$G_{\text{max,LSC}} \approx \frac{\epsilon_2^3}{\epsilon_1^3} \exp \frac{\epsilon_1 - \epsilon_2}{kT},$$

(1.7)
where $k_B$ is the Boltzmann constant and $T$ is the temperature. According to equation 1.7, the maximum concentration factor is intimately related to the Stokes shift, $\Delta \varepsilon = \varepsilon_1 - \varepsilon_2$. For an a LSC based on a dye system whose peak absorption occurs at $\lambda_1 = 600 \text{ nm}$ and whose peak emission is at $\lambda_2 = 700 \text{ nm}$, the maximum concentration factor is $G_{\text{max, LSC}} = 7.7 \times 10^4$. Increasing the Stokes shift by choosing an absorption maximum at $\lambda_1 = 550 \text{ nm}$ while keeping $\lambda_2 = 700 \text{ nm}$ yields $G_{\text{max, LSC}} = 1 \times 10^8$.

Importantly, the maximum concentration factor predicted by equation 1.7 is independent of the direction of the incident light. Theoretically, LSCs can achieve high $G$ without tracking the sun.

In practice, the important loss mechanism known as self-absorption will lead to limitations of the concentration factor. The dyes typically employed in LSCs have broad absorption and emission bands that overlap to some degree, causing radiation to be re-absorbed in the plate. This process has the effect of degrading the high concentrations promised by Eq. 1.7. We discuss this effect in more detail in section 1.3.6.

### 1.3.6 The operational losses of LSCs

The measured flux gains in LSCs are several orders of magnitude lower in practice than the theoretical maximum concentration factor predicted by Eq. 1.7 [16, 18, 19]. Loss mechanisms limit the performance of real LSCs and account for the discrepancy. The performance of a real LSC can be parameterized by the LSC efficiency, $\eta_{LSC}$. We will discuss the most important losses that limit $\eta_{LSC}$ below.

Firstly, some energy will be lost as heat if the photoluminescence quantum efficiency, $\eta_{PL}$, of the dye is less than 100%. Recent advances in the OLED industry have led to huge improvements in this area, such that many currently available dyes have $\eta_{PL}$ approaching unity, especially in the visible part of the spectrum. Selecting a dye with a high $\eta_{PL}$ is a requirement for a high-performance LSC. Secondly,
ergy is lost due to the Stokes-shift between the peak absorption and peak emission of the down-conversion process, $\Delta \varepsilon = \varepsilon_1 - \varepsilon_2$ (see Section 1.3.5), because it reduces the overlap of the LSC absorption with the solar spectrum. Note that this loss is wavelength dependent, since the distribution of solar power varies with wavelength. Thirdly, energy is lost to escaped photons because the trapping of the re-emitted light is imperfect, represented by the trapping efficiency, $\eta_{\text{trap}}$. Conventional LSCs employ randomly aligned dye molecules or atoms that collectively emit their radiation isotropically. A fraction of the re-emitted photons, represented by gray arrows in Fig. 1-6(a), is lost when they are emitted above the critical angle of the waveguide and consequently escape through the face of the LSC. $\eta_{\text{trap}}$ is given by $\sqrt{1 - 1/n_w^2}$, where $n_w$ is the refractive index of the waveguide. For $n_w = 1.5$, 25% of the re-emitted photons are lost. In Chapter 3 we will discuss trapping losses in detail.

Another group of operational losses can be identified as transport losses because they scale directly with $G$. As a photon propagates within an LSC, it can be re-absorbed by other dye molecules if a finite overlap exists between the absorption and emission spectra of the dyes, as illustrated in Figure 1-9. A re-absorption event implies that a new round of PL and trapping losses are incurred; the LSC efficiency consequently decreases exponentially with the number of re-absorption events, $n$: $\eta_{\text{LSC}} \sim (\eta_{\text{PL}} \eta_{\text{trap}})^n$. We note that enhancing LSC performance often implies trade-offs. Increasing the Stokes shift, which allows $G$ to be enhanced, comes at the cost of narrowing the spectrum of light that can be absorbed. The net benefit of using a particular Stokes shift is measured by the product of $G$ with $\eta_{\text{LSC}}$. In general, transport losses have historically limited the flux concentration factors of LSCs to $< 10$ [16, 5, 19, 29, 18] and have been a major obstacle to the commercialization of LSC technology.
1.3.7 Engineering the optical properties of LSCs at the molecular scale

Each loss mechanisms has a distinct microscopic source. Opportunities for improving LSC technology lie in the tackling the sources of loss at the molecular scale. In this thesis, we tailor the optical properties of LSCs to directly address the two most significant loss mechanisms of LSCs; self-absorption and trapping losses.

1.4 Thesis roadmap

This thesis is organized as follows:

Chapter 2 presents a biologically inspired strategy for reducing self-absorption losses. We demonstrate LSCs employing phycobilisomes - photosynthetic antenna complexes that concentrate excited states in red algae and cyanobacteria. The phycobilisomes are cast in a solid-state matrix that preserves their internal Forster energy-transfer pathways and large wavelength shift between absorption and emission. Casting is a simple fabrication technique that also eliminates any need for expensive high-index glass or plastic. By comparing the performance of intact and partly decoupled complexes, we establish that energy transfer within intact phycobilisomes
reduces LSC self-absorption losses by approximately (48±5)%. These results suggest that phycobilisomes are a model for a new generation of cast LSCs with improved efficiency at high optical concentrations.

Studies focused on improving the trapping efficiency of LSCs is the subject of Chapter 3. Ideally, the dyes re-emit the absorbed light into waveguide modes that are coupled to solar cells. But some photons are always lost, re-emitted through the face of the LSC and coupled out of the waveguide. In this work, we improve the fundamental efficiency limit of an LSC by controlling the orientation of dye molecules using a liquid crystalline host. First, we present a theoretical model for the waveguide trapping efficiency as a function of dipole orientation. Next, we demonstrate an increase in the trapping efficiency from 66% for LSCs with no dye alignment to 81% for a LSC with vertical dye alignment. Finally, we show that the enhanced trapping efficiency is preserved for geometric gains up to 30, and demonstrate that an external diffuser can alleviate weak absorption in LSCs with vertically-aligned dyes.

In Chapter 4 we describe a new strategy for harvesting energy in displays. Linearly Polarized Luminescent Solar Concentrators (LP-LSCs) have the potential to replace conventional, purely absorptive, linear polarizers in energy harvesting applications. We introduce light-emitting molecules that are linearly aligned into the matrix of the polarizer so that absorbed photons are not merely dissipated as heat, but are re-emitted within a part of the polarizer that acts as a waveguide, just as in a conventional LSC. As a proof of concept, we align 3-(2-Benzothiazolyl)-N,N-diethylumbelliferylamine (Coumarin 6) and 4-dicyanomethyl-6-dimethylaminostiryl-4H-pyran (DCM) dye molecules linearly in the plane of the substrate using a polymerizable liquid crystal host. We show that up to 38% of the photons polarized on the long axis of the dye molecules can be coupled to the edge of the device for an LP-LSC based on Coumarin 6 with an order parameter of 0.52. We also discuss our work on extending the absorption of the LP-LSC over the full visible spectrum.
In Chapter 5 we present an investigation into the fundamental role that optical waveguiding and exciton diffusion play in transporting triplets within crystalline tetracene and rubrene. We create triplet excitons via the fission of singlet photoexcitations and we study the time- and spatially resolved triplet distribution by monitoring delayed fluorescence, which results when two triplets collide to create a singlet exciton. Our technique allows us to directly image the triplet transport in the a, b and c crystallographic directions of crystalline tetracene and rubrene with sub-micron resolution. Pump-intensity-dependent measurements reveal that at higher initial singlet densities (above $10^{18}$ cm$^{-3}$), transport of triplets through crystalline tetracene and rubrene is dominated by optical waveguiding, a relatively inefficient process that is not likely to be practical in solar cells. Here, two triplets fuse to form a singlet exciton that emits a photon that is waveguided through the crystal and re-absorbed after several microns. We support our measurements by an optical model that simulates the triplet and singlet densities as a function of pump intensity.

Chapter 5 summarizes our findings and suggests future work.

The Appendix presents our work on employing a microcavity to optimize the color of a phosphorescent organic light emitting device (OLED) based on the sky blue phosphor FIrpic. The output of the OLED is filtered by scattering media to correct the angular emission intensity profile and eliminate the angular dependence of the color. With a holographic diffuser as the scattering medium, the microcavity OLED achieves an external quantum efficiency of $(5.5\pm0.6)\%$, as compared to $(3.8\pm0.4)\%$ for a conventional structure. The color coordinates of the microcavity OLED with holographic diffuser are $(x,y) = (0.116\pm0.004, 0.136\pm0.010)$ with minimal angular color shift and a nearly ideal Lambertian angular emission profile.
Chapter 2

Luminescent Solar Concentrators
Employing Phycobilisomes

Reducing the transport losses in LSCs

2.1 Introduction

Loss mechanisms that are associated with optical self-absorption present a serious challenge to maintaining the efficiency of LSCs at increasing values of the geometric gain, $G$. Photons emitted by dyes within the waveguide can be re-absorbed by other dyes within the waveguide when a finite overlap exists between the absorption and emission spectra. A fraction of the re-absorbed photons will be lost to non-radiative decay because the photoluminescence efficiency of dye, $\eta_{PL}$, is less than unity. Furthermore, the isotropic emission profile will cause 25% of the re-emitted radiation to escape the waveguide, assuming its index of refraction is $n = 1.5$. These combined losses, which are compounded at every self-absorption event, can be considerable, and were one of the principal reasons that LSCs were abandoned in the late 70s.

An intriguing strategy for circumventing self-absorption problems can be found in the biological world, where systems have evolved to decouple light harvesting and
energy conversion tasks, analogously to LSCs. Phycobilisomes, in particular, are water soluble biological protein complexes found in red algae and cyanobacteria that funnel solar energy to the photosystem II reaction center, where it ultimately drives chemical reactions. The remarkable phycobilisome structure creates a unidirectional pathway for energy to travel within the complex via Förster energy transfer, resulting in a large shift between the optical absorption and emission maxima. Phycobilisomes also have a high ratio between absorbers and emitters. These optical properties represent a natural strategy for reducing self-absorption in LSCs.

In this Chapter, we study how the arrangement of distinct chromophores in the structure of phycobilisomes promotes successive Förster energy transfers that achieve a large Stokes shift in a highly absorptive, the self-organized complex.

2.1.1 Förster Energy Transfer

Fürster transfer is a fast process by which energy can be transferred from a donor molecule, $D$, in an excited state to an acceptor molecule, $A$, over a relatively long range ($\sim 5 - 10$ nm):

$$D^* + A \rightarrow D + A^*$$ (2.1)

Fürster transfer is a near-field process that occurs without the emission of a photon. It is mediated by dipole-dipole interactions between nearby molecules and is permitted when an overlap exists between the absorption spectrum of the donor molecule with the emission spectrum of the acceptor molecule. (See Fig. 2-1(a) for a schematic representation of Förster transfer).

The Förster rate of transfer, $P_{da}$ (in s$^{-1}$), can be derived from Fermi’s golden rule, and depends on the normalized donor emission spectrum, $f_d(E)$, and the normalized
Figure 2-1: (a) The process of Förster energy transfer. An excited state is transferred from a donor ($D$) molecule to an acceptor molecule ($A$) without the emission of a photon. (b) The acceptor molecule (in red) receives the excited state from the donor molecules (in blue), increasing the shift between absorption and emission spectra of the composite film.

The acceptor absorption spectrum, $F_a(E)$, in the following manner:

$$P_{da} = \frac{3\hbar^3 c^4}{4\pi\epsilon_r^2 R^6} \frac{\alpha_a}{N_a \tau_d} \int \frac{f_d(E)F_a(E)}{E^4} dE.$$

(2.2)

Here, $\epsilon_r$ is the relative dielectric constant, $R$ is the distance between the donor and acceptor molecule, $c$ is the speed of light, $\hbar$ is the reduced Planck constant, $\alpha_a$ is the total absorption coefficient of the acceptor (m$^{-1}$), $N_a$ is the density of acceptor molecules, $\tau_d$ is the mean lifetime of the donor, and $E$ is the photon energy. According to Equation 2.2, the energy transfer rate scales with $R^{-6}$ and is strongly dependent on the overlap between donor fluorescence and acceptor absorption spectrum. Moreover, the rate is inversely proportional to $\tau_d$. $P_{da}$ is conveniently written:

$$P_{da} = \left( \frac{R_0}{R} \right)^6 \frac{1}{\tau_d}.$$

(2.3)

where $R_0$ is the effective Förster radius

$$R_0^6 = \frac{3\hbar^3 c^4}{4\pi\epsilon_r^2 N_a} \int \frac{f_d(E)F_a(E)}{E^4} dE.$$

(2.4)
From equation 2.3 it becomes clear that the transfer of energy between two molecules is very efficient when $R < R_0$, where the distance between the donor and acceptor molecules is $R$. $R_0$ typically ranges between 50 Å and 100 Å.

2.1.2 Reducing self-absorption using Förster energy transfer

Förster transfer can be used to enhance the wavelength shift between absorption and emission spectra of an LSC. The key is the introduction of a low concentration of acceptor molecules that accept excited states from the surrounding donor material; see Fig. 2-1(b). The low density of acceptor molecules takes over the light-emission function within the LSC, shifting the emissive wavelength away from the peak of the LSC absorption. Hence, the energy is gathered by the acceptor molecules using Förster energy transfer[35, 36, 37] if there is sufficient overlap in the absorption and emission spectra of the donor and acceptor molecules, and if the donor and acceptor molecules are within the Förster radius $R_0$ from each other.

The bulk of the LSC can then be classified as donor molecules whose function is to absorb light and transfer the energy to the acceptors. To minimize the losses associated with re-absorption by the acceptor, we must maximize the donor to acceptor ratio. Consequently, we must pack as many donor molecules as possible within the energy-harvesting range of every acceptor molecule, typically just 3-5 nm[35, 36].

There are two methods to control the intermolecular spacing: 1) Deposit the donor and acceptor molecules in a thin film (~1μm) on a waveguide. This approach draws on organic-semiconductor-device technology and is known as an Organic Solar Concentrator (OSC)[19]. The substrate has to be very transparent glass or plastic, and it must have a higher refractive index than the film to prevent optical trapping in the organic layer. 2) Employ aggregates of dyes where multiple donor molecules are positioned within the Förster radius of relatively few acceptors.

The second approach is compatible with the traditional LSC structure where dyes
are cast at low density within a polymer matrix. Casting LSCs eliminates any need for expensive high-index glass, motivating our work on Förster-coupled dye aggregates in the form of phycobilisomes.

### 2.2 Phycobilisomes

![Diagram of phycobilisomes](image)

Figure 2-2: Nature separates the optical and electrical tasks in energy harvesting by using antennas to harvest photons and to funnel this energy to the reaction center embedded in a lipid bilayer, where it is converted in chemical energy. Phycobilisomes (PBSs) are an example of such an antenna system to photosystem II in cyanobacteria and red algae. They are capable of absorbing light in the 500-650 nm range, which are inaccessible to PSII.

The decoupled optical and electrical functions of LSCs and their attached solar cells, respectively, are analogous to the separate light collection and charge generation tasks in photosynthesis[38]; (see Figure 2-2). Indeed, photosynthesis employs various light-collection structures that may be used in LSCs. In this work, we report solution-based and solid-state LSCs that use phycobilisomes[39, 40]. Phycobilisomes are large water-soluble pigment-protein complexes that function as light-harvesting devices in red algae and cyanobacteria. They are capable of absorbing light over a broad range of the visible spectrum and efficiently concentrating this captured energy at the photosynthetic reaction center; see Figure 2-2.

The main components of phycobilisomes are phycobiliproteins, which serve as
Figure 2-3: (a) A schematic representation of the structure of a phycobilisome - a macromolecular protein complex[39]. Hemispherically organized rods of phycocyanin (PC) and/or phycoerythrin (PE) biliproteins join a core of allophycocyanin (APC) biliproteins. The bulk of the absorption takes place in the rods, while the unique nanostructure facilitates energy transfer towards the core of the complex, resulting in a large Stokes shift. (b) Each biliprotein serves as a scaffold for its own characteristic chromophores, which are spatially arranged through self-assembly. Presented here is the structure of APC. The red and blue units are representing the 2 types of chromophores that can be found in an APC biliprotein. Picture taken from [41].

scaffolding for covalently bound, linear tetrapyrrole chromophores called bilins[42], see Figure 2-3(b). The chromophores are arranged through self-assembly in cascading Förster-energy-transfer pathways that couple short wavelength chromophores at the extremities of the complex to long wavelength chromophores at the core of the complex. The phycobilisome core is composed of allophycocyanin (APC) (see Figure 2-3(a)) containing approximately 72 chromophores (phycocyanobilin) that absorb at \( \lambda_{\text{max}} = 650 \text{ nm} \). Depending on the organism, 4-6 phycocyanin (PC) radial rods
are attached to the core, each rod contains approximately 18 chromophores (phyco-
cyanoobilin) absorbing at $\lambda_{max} = 620$ nm. Finally, in some organisms, the PC rods are capped by additional rod structures containing phycoerythrin (PE) with approximately 34 chromophores (phycoerythrobilin or phycourobilin) that absorb at either $\lambda_{max} = 545$ nm or $\lambda_{max} = 490$ nm. The quantum efficiency of energy transfer within the phycobilisome complex typically exceeds 95%[43]. But when decoupled, energy transfer is prevented and the chromophores emit light. The photoluminescent (PL) efficiency varies between $\eta_{PL} = 98\%$ for PE, $\eta_{PL} = 51\%$ for PC, and $\eta_{PL} = 68\%$ for APC [43]. See Figure 2-4 for the PL spectra of the three types of bilins that are found in different parts of the phycobilisome. Notice how widely separated in energy they are.

![Figure 2-4: The PL spectra of the three types of phycobiliproteins used in this study.](image)

The total number of bilins per phycobilisome is highly variable between different
species and even within a species under different growth conditions[45], see Fig. 2-5. A typical estimate for the ratio of chromophores in PE, PC and APC is 408:108:72, i.e. the ratio of donor to acceptor molecules is approximately 6:1 in phycobilisomes. This is lower than the 30:1 ratio reported in [19]. But the high ratio in ref. [19] is due to the high density of donors, which increases the refractive index of the film to \( n = 1.7 \) and possibly necessitates the use of a more expensive substrate.

2.3 Experimental Section

2.3.1 Phycobilisome preparation

The phycobilisomes used for this study were prepared by our collaborators Mark Moss, Clifford McLain, John Morseman from Columbia Biosciences Corporation and Michael Vaughn, Paul Willard and Barry Bruce from the University of Tennessee at Knoxville. Here to follow is a description of the methods used to grow, isolate, and stabilize the three types of phycobilisomes that were employed in our experiments:

- A stabilized, fully coupled phycobilisome with three types of biliproteins (PE-PC-APC);

- A partially coupled complex with two types of biliproteins (PC-APC);

- A fully decoupled complex with the same two types of biliproteins (PC-APC).

Intact phycobilisomes containing B-Phycoerythrin (B-PE), R-Phycocyanin (R-PC) and Allophycocyanin (APC) were isolated from the organism Porphyridium cruentum. Cultures of P. cruentum were grown using a nutrient-supplemented media designed to replicate conditions in seawater, in a controlled environment photobioreactor under low light (< 1000 lux) and high nitrate (> 500 mg/liter) conditions in order to induce a high level of phycobilisome production. Cultures were harvested
after 4 weeks of growth by continuous flow centrifugation. The biomass was resuspended in 0.75M potassium phosphate, pH 7.4 (KPI) to maintain the appropriate ionic strength needed for intact phycobilisomes. The cells were disrupted by microfluidizer and cell wall debris and insoluble starches were removed by centrifugation. Intact phycobilisomes were then treated with a 1% (w/v) solution of detergent (Triton X-100, Sigma-Aldrich) in KPI buffer to solubilize and remove chlorophyll from the terminal emitter APC. After extraction of the chlorophyll, the phycobilisomes where precipitated by the addition of 20% (w/v) PEG 8000 (Sigma-Aldrich) followed by centrifugation at 4700 x g to pellet the phycobilisomes. The resulting pellet was resuspended overnight in 0.75M KPI and purified by gel filtration column chromatography using CL-6B Sepharose resin (GE-HealthCare). This step purified uncoupled phycobiliproteins, other cellular proteins, and protein aggregates as well as any residual chlorophyll away from the phycobilisomes. The purified phycobilisomes were then treated with 1% (v/v) formaldehyde overnight and quenched with 1% of a 1M solution of lysine, pH 7.2 (Sigma). The stabilized phycobilisomes were purified again over Sepharose CL-6B resin in 0.1M sodium phosphate, pH 7.4 to remove any residual uncoupled phycobiliproteins and protein aggregates formed during the stabilization. The material was then freeze dried in 0.1M sodium phosphate, pH 7.4 with 0.2 M sucrose (Sigma-Aldrich). The non-PE containing PBS from Synechocystis PCC6803 were isolated using sucrose gradient centrifugation essentially as described in reference [42]. To study the effect of chromophore coupling on the LSC performance, unstabilized phycobilisomes were decoupled by diluting them in a 0.1 M phosphate buffer. At such low salt concentrations, the destabilized phycobilisomes decompose fully into their separate APC and PC proteins[46].
2.3.2 Solid-state phycobilisome waveguide

Casting method

Figure 2-6: (a) Photograph of a cast polyacrylamide film that incorporates intact phycobilisomes consisting of fully coupled phycoerythrin, phycocyanin and allophycocyanin biliproteins. (b) Schematic representation of the measurement set up used to determine the Optical Quantum Efficiency (OQE) of the phycobilisome film. The film ($n_S = 1.6$) was cast upon a high index glass substrate ($n_S = 1.7$, Scott SF10 glass), and characterized in an integrating sphere to measure its edge emission as a function of excitation wavelength.

To cast phycobilisomes in solid-state waveguides, they must be incorporated within a matrix that mimics the native aqueous environment, while simultaneously providing a rigid substrate. Polyacrylamide hydrogels satisfy both requirements[47, 48, 49]. To increase the rigidity of the matrix we used a lower water content than is normally used in polyacrylamide films for gel electrophoresis. To decrease stress in the film, we added an extra monomer with bulky groups, N-isopropyl acrylamide (NIPAM), to the acrylamide monomer to increase steric repulsion between chains. We also decreased the ratio of the crosslinker (bis-acrylamide) to yield a lower crosslinking density. Equal portions of a 40% (w/v) water based solution of 37.5:1 acrylamide/bisacrylamide solution (Sigma-Aldrich) and a 40% (w/v) solution of NIPAM (Sigma-Aldrich) in deionized water was mixed thoroughly using a mini-vortexer (VWR). To this solu-
tion, a freshly prepared solution of ammonium persulfate (Sigma-Aldrich) was added up to a concentration of 1% (w/v) and vigorously mixed. In a separate vial, dry phycobilisomes were rehydrated with 100μl of 0.1M phosphate buffer, and to this solution a 1 ml solution of the monomeric acrylamide solution was added. To accelerate the polymerization 1.5 μl of TEMED (N,N tetramethylethylene diamine) (Sigma-Aldrich) was added. After gentle mixing, the resultant solution was allowed to polymerize at room temperature in a mini-hybridization chamber (Electron Microscopy Sciences). This resulted in smooth, flexible, optically clear films with a refractive index of n = 1.6[50] potentially compatible with polycarbonate substrates. The films were square with length L = 22 mm, a thickness of t = 0.5 mm (see Figure 2-6(a)).

**Optical Characterization**

To enable characterization, the optically smooth phycobilisome film was supported on a glass slide. We did not observe the transmission of phycobilisome photoluminescence into the glass substrate, probably due to the presence of an air gap between the gel and the glass. The integrity of phycobilisomes in the films was examined by comparing the absorption and fluorescence spectra of phycobilisomes in films and in phosphate buffer, see Figure 2-7. All thin film absorption measurements were obtained using an Aquila spectrophotometer, while the fluorescence spectra of facial emission from LSCs were obtained using a 408 nm laser as an excitation source. The film absorbed 70% of the incident light at the peak absorption wavelength of λ = 545 nm, and the emission was measured from the face of the sample. Both the emission spectra in the phosphate buffer and in the acrylamide film show strong emission from APC and almost complete quenching of PE emission at λ_{max} = 572 nm[39], suggesting the internal energy-transfer path is largely preserved. In the absence of packaging, the gels dry out and lose their smooth morphology within several hours, increasing optical scattering losses and obscuring the observation of possible phycobilisome photodegradation. Thus, all
characterization was performed immediately after fabrication.

Figure 2-7: The OQE (blue dots) and normalized photoluminescence (red solid line) of the acrylamide phycobilisome (PE-PC-APC) films. The similarity of these data with the absorption and photoluminescence spectra of the phycobilisome complexes in phosphate buffer (dotted lines) demonstrates that the optical properties of the phycobilisomes are well preserved in the solid state film.

The Optical Quantum Efficiency

The optical quantum efficiency, $\eta_{\text{edge}}$, defined as the fraction of incident photons that is emitted from the edges of the OSC substrates, was characterized within an integrating sphere; see Figure 2-6(b). Edge and facial LSC emission is discriminated by selectively blocking the edge emission with black tape and a black marker. These spectrally-resolved measurements employed a 150W Xenon lamp coupled into a monochromator and chopped at 80 Hz. The photoluminescence for the OQE measurements was detected by a Si photodetector mounted directly on the integrating sphere. The spectrally-resolved OQE is compared to the absorption of complexes in phosphate buffer in Figure 2-7. The OQE of the film as a function of excitation wavelength matches the absorption spectrum of phycobilisomes in their native environment, confirming that the optical properties of the phycobilisomes are well pre-
served in the solid state. The peak $\eta_{\text{edge}} = 12.5\%$ compares to peak efficiencies exceeding $\eta_{\text{edge}} = 50\%$ in organic solar concentrators that use thin-film coatings of synthetic dyes[19]. The lower performance of cast phycobilisome-based LSCs is due to an absorption of only 70% of the incident light in the 0.5-mm-thick LSC at the peak absorption wavelength of 560 nm, the observation of a relatively low photoluminescent efficiency for APC in the films ($\eta_{\text{PL}} < 50\%$) and significant facial emission ($\eta_{\text{face}} = 12\%$), probably due in part to scattering at the interface between the film and its glass substrate. This is consistent with optical reflection and transmission measurements of the gels which yield an upper limit of 3% per mm for the scattering loss in the glass bilayer. The low photoluminescent efficiency ($\eta_{\text{PL}} < 50\%$) relative to previous measurements[43] of APC ($\eta_{\text{PL}} = 68\%$) could be due to incorporation in the solid state film.

2.3.3 Transport losses and Förster energy transfer

Next, we examine the effect of Förster energy transfer on self-absorption losses within the phycobilisome-based LSCs. To eliminate any effects due to stress in the solid state films, we performed these measurements in aqueous LSCs whose picture is shown in Figure 2-8(a) and schematically in Figure 2-8(b). 1-mm-thick sheets of glass (Erie Scientific, $n = 1.5$) were cut and glued together with epoxy (Epo-Tek 301, Epoxy Technology) to form an aquarium with dimensions of 7.6 cm $\times$ 7.6 cm $\times$ 0.34 cm. A GaAs solar cell from Spectrolab with an external quantum efficiency (defined as electrons out per photon in) of $\sim 90\%$ was cut into a 3.8 cm $\times$ 0.34 cm strips. Two of these cells were connected in series, and attached to the edge of the concentrator with index matching fluid (Norland Products). The other 3 edges were blackened out to prevent indirect luminescence from reaching the solar cell. These spectrally-resolved measurements employed a 150W Xenon lamp coupled into a monochromator and chopped at 20 Hz. Geometric gain dependent measurements were obtained by
directing the excitation beam perpendicular to the LSC so as to create a spot of
\(~1\) mm\(^2\), while the distance, \(d\), between the spot and the solar cell was varied; see
Figure 2-8(a) and (b). The measured photocurrent was multiplied by the factor, \(g\),
that corrects for the different angle subtended by the solar cell at each spot distance:

\[
g = \frac{\pi}{\tan^{-1}(\frac{L}{2d})}
\]

, where \(L\) is the length of the edge of the LSC. This is an experimentally conve-
nient technique to simulate the performance of LSCs at different geometric gains. It
provides a lower bound for the performance since the average optical path-length is
slightly longer than a uniformly illuminated LSC.

The phycobilisome solution was diluted in a 0.75M phosphate buffer (pH 8.0)
until the solution had an absorbance of 0.5 over a path length of 1 cm at the peak
absorption wavelength. All liquid based LSC measurements employed a mirror behind
the LSC to add a second pass of pump radiation within the LSC. See Figure 2-8 for
a picture and a schematic of the set-up.

**Förster energy transfer and self-absorption**

The water-based LSCs employed three types of phycobilisomes, a stabilized, fully cou-
pled phycobilisome with three types of biliproteins (PE-PC-APC), a partially coupled
complex with two types of biliproteins (PC-APC), and a fully decoupled complex with
the same two types of biliproteins (PC-APC). The stabilized phycobilisomes remain
stable in solution up to one year at 4°C[51]. The absorption and emission spectra of
these phycobilisome complexes are shown in Figure 2-9(a). The fluorescence spectra
were obtained using a 408 nm laser as an excitation source. The fully coupled com-
plexes possess an abundance of PE, leading large Stokes shifts between the emission
of APC at \(\lambda = 680\) nm and the peak absorption of PE at \(\lambda = 545\) nm. The partially
coupled and fully decoupled complexes show smaller Stokes shifts. The absorbance of the partially coupled and fully decoupled PC-APC phycobilisome complexes peaks at a wavelength of $\lambda = 620$ nm, where the PC protein has its peak absorption. The partially coupled PC-APC phycobilisomes show no evidence of PC fluorescence at $\lambda = 650$ nm, suggesting full energy transfer to APC. For the decoupled complex, however, the observed emission is mostly due to decoupled PC chromophores that emit at $\lambda = 650$ nm.

**Förster energy transfer and the performance versus optical concentration**

The external quantum efficiency (EQE) as a function of geometric gain, $G$, for the liquid LSCs is presented in Figure 2-9(b). The geometric gain is defined as the ratio of the facial area to the area of the edges and is a key LSC parameter. It measures the path length of photons within the waveguide, and it determines the maximum possible optical concentration in the LSC. Typically, re-absorption losses increase
with $G[19]$. The EQE was measured at $\lambda = 620$ nm for the partially coupled and fully decoupled complexes, and at $\lambda = 550$ nm for the fully coupled complexes containing PE. Consistent with the absorption and emission data, the Förster-coupled complexes are observed to have the best performance at higher geometric gain. The lower value of the EQE of the water-based LSCs compared to the OQE of the acrylamide films ($G = 11$) is due to a lower absorption coefficient, a lower trapping efficiency of the water-based system, loss due to coupling to the solar cell and loss due to the non-unity EQE of the solar cell.

To quantitatively compare the different complexes, we define the self-absorption loss as the decrease in EQE as a function of geometric gain relative to the EQE at $G = 1.4$. A direct comparison is easiest between the fully coupled and partially decoupled complexes since they both emit from APC. Over all measured geometric gains, the intact phycobilisome complexes exhibit a self absorption loss that is $(48\pm5)\%$ lower than the partially decoupled phycobilisomes. The fully decoupled complexes have the highest self-absorption losses of all due to the absence of energy transfer and the resulting emission by both PC and APC, resulting in a smaller Stokes shift.

### 2.4 Conclusions

To conclude, the unique self-assembled nanostructure phycobilisomes that couples a large number of donor molecules through an internal Förster energy pathway to a handful of acceptors, reduces re-absorption losses in LSCs by approximately 50%. Thus, phycobilisomes provide a structural model for synthetic dyes in a new generation of cast LSCs with improved performance at high optical concentrations. In addition, we have also demonstrated that phycobilisomes themselves can be stabilized in a solid-state LSC matrix with minimal loss of performance. Future phycobilisome-based devices may be significantly improved by coupling efficient synthetic dyes to APC
(see for instance commercial products available from Molecular Probes). Additionally, the ratio of donor to acceptor pigments can be increased by selecting organisms with a better endogenous pigment ratio (either naturally occurring or through directed evolution)[52]. Finally, the protein environment of the terminal pigment can be molecular engineered to further improve the photostability and thermostability of phycobilisomes[53].
Figure 2-9: (a) The absorption and emission spectra of the phycobilisome complexes employed in the water-based LSCs. The green lines correspond to the fully coupled phycobilisome with three types of biliproteins (PE-PC-APC). The absorption of the partially coupled PC-APC complexes and the fully decoupled PC-APC are identical (dashed red line and solid blue line respectively). The emission spectrum of the decoupled complex is dominated by the PC emission (solid blue), while the emission of the partially coupled complex results from the APC bilins (dashed red line). The Stokes shift is largest for the fully coupled complex consisting of PE-PC-APC, while the decoupled complex has the largest overlap between absorption and emission spectrum. The self-absorption ratio, S, defined as the ratio between the peak absorption and the absorption at the peak emission wavelength[19] is 17.5, 10.1 and 1.7 for the fully coupled, the partially coupled and the decoupled complexes respectively. (b) The external quantum efficiency versus geometric gain, G, of the water-based LSCs employing fully coupled phycobilisomes with three types of biliproteins (PE-PC-APC) (green line), the partially coupled PC-APC phycobilisomes (red line), and the fully decoupled PC-APC phycobilisomes (blue line). The fully coupled complex has the best performance with geometric gain, reflecting its large Stokes shift, and hence reduced self-absorption losses.
Chapter 3

Dye Alignment in Luminescent Solar Concentrators: I. Vertical Alignment for Improved Waveguide Coupling

3.1 Introduction

The focus of this Chapter is the trapping efficiency of photons in the waveguide. Imperfect trapping represents another fundamental loss of LSCs, for which large improvements are still possible.

3.1.1 The Origin of trapping losses in LSCs

Conventional LSCs employ randomly aligned dyes that collectively emit photons isotropically on average; see Fig. 3-1(a). Trapping losses are incurred when photons are re-emitted towards the face of the waveguide with an incident angle above the critical angle for total internal reflection, \( \theta_C \). As can be seen in Eq. 3.1, \( \theta_C \)
depends on the refractive index of the substrate, \( n_S \), and the cladding, \( n_C \):

\[
\theta_C = \cos^{-1} \sqrt{1 - \frac{n_C^2}{n_S^2}}
\]

Calculating the fraction of the total power that is emitted into the critical escape cone, we find that 25\% of all the photons are lost through the face for \( n_S = 1.5 \). And this is only for one re-emission event – after 2 such events, only 42\% of the photons remain trapped, so the problem becomes compounded. In section 3.2 we will discuss the theoretical calculations for the trapping efficiency in detail.

One way to reduce these trapping losses is to reduce the critical angle, which means increasing the refractive index, \( n_S \). In Section 3.2 we will show that this strategy is unlikely to result in a trapping efficiency above 95\% using on low cost materials. Another approach is to use mirror systems, such as dielectric mirror stacks, to keep the photons trapped in the waveguide. But such mirrors are hard to make on a large scale, expensive, and perform poorly off angle.

### 3.1.2 Increasing the trapping efficiency by aligning dichroic dyes

In this work we focus on the source of the problem, the dye emission pattern in itself. We control the pattern of radiation coming from the dyes so as to increase the fraction of the total power emitted below the critical angle, see figure 3-1(b). For this we make use of the luminescent properties of dichroic dye molecules.

A dichroic dye molecule is long and rod shaped, and looks like an antenna, like coumarin 6 in Fig. 3-1(c). Electrically, it behaves like one, too and it can be modelled as a dipole. We can make use of the fact that the radiation pattern of dipoles is anisotropic, with most of the power emitted normal to the axis of the dipole, see Fig. 3-1(a).
Figure 3-1: (a) The emission profile of isotropic dipoles and a linearly aligned, anisotropic dipole. The absorption and emission profile of isotropic dipoles is uniform, while the anisotropic dipole emission is characterized by a \( \sin^2 \theta \) profile, with little power emitted along the long axis of the dipole molecule. (b) In order to improve the performance of LSCs, we align dichroic dye molecules perpendicular to the waveguide, enhancing the fraction of the total dipole power emitted below the critical angle \( \theta_c \), and hence trapped within the waveguide. (c) An example of a dichroic dye molecule, Coumarin 6.

Following the suggestion of Debije et al.[54] we directly address trapping losses by controlling the orientation of the dye molecules vertically with respect to the waveguide so their transition dipoles couple more strongly into the waveguide, as illustrated in Figure 3-1(b). We employ a homeotropic liquid crystal matrix to align rod-shaped dye molecules perpendicular to the waveguide, as illustrated in Figure 3-2. Orienting the molecules at a right angle to the surface reduces the absorption of perpendicular incident radiation. Consequently, we employ an optical diffuser above the LSC to scatter incident light.

### 3.1.3 Chapter Outline

First, we derive theoretical predictions for the trapping efficiency as a function of the refractive index of the waveguide and the angle of the transition dipole. We also derive an expression for \( \eta_{trap} \) of an isotropic LSC as a function of the angle of the incident
Figure 3-2: A polymerizable liquid crystal host serves as a scaffold for dichroic dye molecules that are aligned perpendicular with respect to the waveguide. These vertically aligned dipoles couple more strongly into guided waveguide mode, resulting in an enhanced trapping efficiency. An external diffuser is used to correct for the reduced ability to absorb light incident perpendicular to the waveguide.

light. Second, the trapping efficiency is determined experimentally for both vertically aligned and isotropic dye systems and compared to theoretical predictions. We demonstrate that vertically aligned (homeotropic) LSCs employing the rod shaped dye molecule, Coumarin 6 (3-(2-Benzothiazolyl)-N,N-diethylumbelliferylamine) exhibit higher efficiencies than conventional LSCs that rely on isotropic Coumarin 6 in a PMMA (poly(methyl-methacrylate)) host matrix. Third, the performance of the LSCs as a function of incident angle is studied for the vertically aligned dipoles and contrasted to the performance of the isotropic system. Furthermore, the effect of the addition of an external diffusing layer to the vertically aligned and isotropic LSCs is characterized. Finally, the overall efficiency of the isotropic and vertically aligned LSCs is assessed as a function of geometric gain and compared to Monte Carlo simulations based on LSCs employing isotropic and homeotropically aligned dye systems.
3.2 Trapping Efficiency - Theoretical Predictions

To assess the effect of dye molecule alignment on the trapping efficiency of LSCs, we first assume that a transition dipole aligned parallel to the long axis of the molecule determines the molecular emission pattern. We then calculate the fraction of photons trapped in a waveguide as a function of dipole orientation, $\theta_D$, and the refractive index of the waveguide, $n_S$, and cladding media, $n_C$.

The expression for the time-averaged power density of a Hertzian dipole oriented along the z-axis [55] can be extended to arbitrary inclination, $\theta_D$ (see Figure 3-3 for a schematic representation of the dipole orientation). The obtained expression for the power density, is integrated over the solid angle from $\theta_C$ to $\pi - \theta_C$, where $\theta_C$ is the critical angle $\theta_C = \cos^{-1}\left(1 - \frac{n_C^2}{n_S^2}\right)$. Normalizing by the total power emitted by the dipole yields the following expression for the trapping efficiency of aligned dyes:

$$\eta_{\text{trap}}(\theta_D) = \sqrt{1 - \frac{n_C^2}{2n_S^2}} \left(1 + \frac{n_C^2}{n_S^2} \left[1 - \frac{3}{2} \sin^2 \theta_D\right]\right)$$  \hspace{1cm} (3.2)

The trapping efficiency of aligned dyes as a function of $\theta_D$ is plotted in Figure 3-4(a) for three different waveguide-refractive indexes. The trapping efficiency is maximum for a dipole aligned with the z-axis ($\theta_D = 0^\circ$), varying from $\eta_{\text{trap}} = 91\%$ for a dipole embedded in a $n_S = 1.5$ medium to $\eta_{\text{trap}} = 95\%$ for $n_S = 1.7$. The calculations assume an air cladding ($n_C = 1$). The lowest trapping efficiency is calculated for a dipole lying in the plane of the waveguide ($\theta_D = 90^\circ$), ranging from $\eta_{\text{trap}} = 66\%$ for $n_S = 1.5$ to $\eta_{\text{trap}} = 73\%$ for $n_S = 1.7$.

Figure 3-4(b) presents the calculated trapping efficiency as a function of $n_S$ for perpendicular, in-plane and isotropic dipoles. Achieving $\eta_{\text{trap}} > 90\%$ in an LSC based on isotropic, randomly-oriented dye molecules, requires a waveguide with refractive index $n_S > 2.2$. The practicality of the various approaches to improving trapping efficiency is discussed below. The trapping efficiency of an isotropic dye system can
Figure 3-3: Schematic representation of the dipole orientation within the waveguide of the LSC. The angle between the dipole moment, \( \vec{d} \), and the electric field vector, \( \vec{E} \), of the excitation beam, \( \vec{k} \), is defined as \( \varphi \).

Also be calculated from Eq. 3.2. Assuming that the exciton alignment within the LSC is also isotropic yields the familiar result for the isotropic trapping efficiency:

\[
\eta_{\text{iso}} = \int_0^{\pi/2} d\theta_D \sin \theta_D \sqrt{1 - \frac{n_C^2}{2n_S^2} \left(1 + \frac{n_C^2}{n_S^2} \left[1 - \frac{3}{2} \sin^2 \theta_D \right]\right)} = \sqrt{1 - \frac{n_C^2}{n_S^2}} \tag{3.3}
\]

**Trapping efficiency vs angle incident light**  However, if there is no energy transfer or other dispersion of exciton alignment within the LSC, then the angular distribution of excited dyes depends on the angle of the incident light, \( \theta_I \), as measured within the LSC [19, 56]. Integrating over all solid angles, and normalizing gives the following expression for trapping efficiency for an isotropic dye system as a function of the angle of the incident light:

\[
\eta_{\text{iso}}^{\text{iso}}(\theta_I) = \frac{\int_0^{2\pi} d\phi_D \int_0^{\pi/2} d\theta_D \eta_{\text{trap}}(\theta_D) \sin \theta_D \cos^2 \varphi}{\int_0^{2\pi} d\phi_D \int_0^{\pi/2} d\theta_D \sin \theta_D \cos^2 \varphi} \tag{3.4}
\]
Figure 3-4: (a) The calculated trapping efficiency as a function of the orientation of a Hertzian dipole with respect to the waveguide for three different refractive indexes of the dye medium. \( \theta_D = 0^\circ \) corresponds to a dipole oriented perpendicular to the waveguide, while \( \theta_D = 90^\circ \) describes a dipole aligned in the plane of the waveguide. (b) The calculated trapping efficiency as a function of the refractive index of the dye medium, \( n_s \), for vertically aligned dipoles (green line), isotropic dipoles (red line) and in-plane aligned dipoles (blue line). We use the conventional Eqn. 3.3 for the trapping efficiency of isotropic dipoles.

\[
\eta_{trap,p}(\theta_I) = \sqrt{1 - \frac{n_c^2}{n_S^2} \left(1 - \frac{n_c^2}{10n_S^2} \left[1 - 3 \sin^2 \theta_I \right] \right)} \quad (3.5)
\]

And for \( s \)-polarized incident light:

\[
\eta_{trap,s}(\theta_I) = \sqrt{1 - \frac{n_c^2}{n_S^2} \left(1 - \frac{n_c^2}{10n_S^2} \right)} \quad (3.6)
\]
Figure 3-5: The calculated trapping efficiency of an LSC for $s$ and $p$ polarized light based on isotropic dipoles as a function of the angle of the incident light, as measured outside of the waveguide with refractive index of $n_S = 1.5$ (blue line) and $n_S = 1.6$ (red line). $\eta_{trap}$ is independent of excitation angle for $s$-polarized light, while $\eta_{trap}$ increases 3-5% from normal till 90° incidence for $p$-polarized light. We also plot $\eta_{trap}$ for the case where the dependence of the angular distribution of excited dyes on the angle of the incident light is not taken into account (dotted red and blue lines) (Eqn. 3.3).

These results appear to differ from those reported previously [56]. The most important consequence of considering the anisotropic initial distribution of excited dipoles is a reduction in the expected trapping efficiency from $\eta_{trap} = 75\%$ for an $n_S = 1.5$ index waveguide under normally-incident light to $\sim \eta_{trap} = 71\%$; see Fig. 3-5.

### 3.3 Device Fabrication

Vertically aligned and isotropic dyes are incorporated in scaffolds of a homeotropic polymerizable liquid crystal mixture or PMMA, respectively. The substrate is a 1-mm-thick glass with a refractive index, $n_S = 1.7$ (SF10, Schott). Glass substrates are cut with a dicing saw to the desired dimensions. The geometric gain, $G$, of an LSC is defined as the ratio of the face area versus edge area. When solar cells are attached to each edge of a square collector, $G = L/4t$, where $L$ is the length of the LSC and $t$ is the thickness. For the experimental assessment of the trapping efficiency the glass
substrates are cut to squares of $2 \times 2$ cm. Measurements of the external quantum efficiency (the fraction of incident photons converted to current in the attached solar cells) employ substrates with a substrate size of $7.6 \times 9.5$ cm. The glass substrates are thoroughly cleaned with a detergent solution, DI water, and solvents.

### 3.3.1 Vertically aligned LSC fabrication

The polymerizable homeotropic liquid crystal host used in this study is UCL018 (Dai Nippon Ink and Chemicals, Inc.). This mixture includes a polymerizable nematic liquid crystal, homeotropic dopant molecules, and a photo-initiator. The dye molecule used for the experiments is Coumarin 6. Coumarin 6 has a high photoluminescence efficiency (measured to be 78%, which is in close agreement with literature [57]) and is known to possess a relatively high dichroic ratio [58]. Coumarin 6 is also characterized by a large Stokes shift, which makes this dye especially suitable in an LSC [59, 29]. In a vial, UCL018 (40%) is added to Coumarin 6 (0.40% total weight $\sim 1\%$ solid weight content). FC-4430 (NovecTM, 3M) is used as a surfactant (0.40%) and taken from a pre-prepared solution of 5% FC-4430 dissolved in toluene. To these substances, toluene is added (59.2%) and gently stirred. All percentages of the separate components are given relative to the total weight of the mixture. When the components are well dissolved (after being stored for approximately an hour in the dark at room temperature) the solution is filtered and spin-cast on the glass substrates. The spin-speed is adjusted to yield a peak-absorption of around 40% (optimized for specific experiments). A typical spin-cast recipe uses an acceleration of 500 rpm/sec and a spin speed of 1250 rpm for a duration of 15 seconds. Directly after spinning, the samples are placed for 1 minute on a hotplate at 50°C in still air. Subsequently, the samples are cooled down to room temperature for 1 minute before placing them under a UV lamp (365 nm) for 2 minutes to cure.
3.3.2 Isotropic LSC fabrication

Isotropic LSCs use PMMA (Sigma Aldrich) as a host matrix. In a vial, PMMA and toluene are added to a concentration of 150 mg/mL. The vials are heated (at 70°) and stirred to dissolve the PMMA. Coumarin 6 is added to obtain a concentration of 1.5 mg per mL of toluene (equal to a 1% solid weight content). After all components are well dissolved the solution is filtered and spin-cast on a clean glass substrate. Also here, the spin-speed is adjusted to obtain the desired peak-absorption within the sample. All thin film absorption measurements are obtained using an Aquila spectrophotometer at 30° incidence.

3.4 Experimental Techniques

3.4.1 Measuring the trapping efficiency

The trapping efficiency of conventional, isotropic LSCs and vertically-aligned LSCs is measured with the use of an integrating sphere (see Fig.3-6(a) for a schematic of the set-up). The samples are placed in the center of the sphere and excited by a monochromatic beam incident normal to the face of the samples. The beam is created by coupling a 150W Xenon lamp into a monochromator and chopping it at 73 Hz. The photoluminescence of the LSCs is detected through a photo-detector mounted on the integrating sphere. The trapping efficiency is given by the ratio between the number of photons emitted from the edges of the LSC to the total number of photons that are emitted from both the face and the edge of the LSC. We discriminate between face and edge emission by selectively blocking the edge emission with a black marker.

We correct for the difference in responsivity of the integrating sphere and the photo-detector for clear edged and black edged samples. The blackening with a black marker is tested to block over 98% of the transmission and internal reflections.
Figure 3-6: (a) A schematic representation of the side-view of the measurement set up used to determine the trapping efficiency, $\eta_{\text{trap}}$, of the LSCs. The isotropic and vertically aligned LSCs are characterized in an integrating sphere to measure the edge and facial emission as a function of excitation wavelength. (b) Schematic representation of the top-view of the set-up used to test the angular dependence of the absorption within isotropic and vertically aligned LSCs. One of the edges of the LSC is placed into an opening of an integrating sphere, which allows the monitoring of the edge emission as a function of the incident angle of the excitation beam. For studies of the effect of an external scattering layer, holographic diffusers are placed in the path of the excitation source at a distance of 1mm from the LSC.

3.4.2 Measuring the angular dependence of the absorption

The angular dependence of the absorption within isotropic and homeotropic (vertically aligned) LSCs is obtained from the edge emission as a function of the angle of the incident light beam. Not only is the fraction of photons emitted from the edge of the LSC directly proportional to the number of photons absorbed within the waveguide, it is the best measure of the performance of the LSC overall. Furthermore, it allows us to probe the angular distribution of excited dyes within the LSC, which, for the isotropic LSCs, will depend on the angle of the incident light. As outlined in Section 3.2, increasing the incident angle will increase the number of excited vertical dipoles and hence result in an enhancement in the trapping efficiency. A schematic
representation of the set-up used to test the angular dependence of the LSC performance is presented in Fig.3-6(b). One of the edges of the LSC is placed into the opening of an integrating sphere, while the other three edges of the glass are blackened out to prevent indirect radiation reaching the edge inserted into the sphere. The LSC is excited in the center of the waveguide with a $\lambda = 408$ nm laser, whose power is monitored over time with the use of a beam-splitter and a second photo-detector. The remainder of the opening in the sphere is blocked and a spectral filter is used to prevent scattered laser light from reaching the photo-detector that has been mounted directly onto the sphere.

Holographic diffusers are obtained from Edmund Optics with 90% transmission efficiency under varying diffusive strengths. The diffusive strength (10°, 30° and 60° for the holographic diffusers used in this experiment) is the maximum angle to which at least 0.1% of the light is scattered given a collimated beam incident normal to the surface. The holographic diffuser is placed at a distance of 1mm in front of the LSC (see Fig.3-6(b)) and the laser beam is positioned to be incident normal to the diffuser surface.

3.4.3 Measuring the performance versus optical concentration

The external quantum efficiency of an LSC, the ratio of electrons out to photons in, is measured with a technique that is discussed in detail in Section 2.3.3. For the aligned LSCs, we used two GaAs solar cells from Spectrolab, each with an external quantum efficiency of 85% and cut into 3.8 cm $\times$ 0.34 cm strips. The cells are connected in series, and attached to one of the short edges of the LSC with index matching fluid (Norland Products). The other 3 edges are blackened out with a black marker to prevent indirect luminescence from reaching the solar cell. The absorption within the films peaked at 42% for both the isotropic and homeotropic LSCs.
3.4.4 Monte Carlo ray tracing model

Experimental results are compared to simulations using a Monte Carlo ray tracing model [60, 61, 62, 63], extended to consider dye molecules with arbitrary orientations. The LSC components are modeled by their experimentally measured spectral absorption coefficients, photoluminescence spectra, photoluminescence quantum efficiency, and refractive indices. In particular, we use the experimentally determined absorption and emission spectra of Coumarin 6, and the glass waveguide is modeled by SF10 parameters\(^1\). The refractive index of the organic film was simulated as \(n_S = 1.5\) for the PMMA film and \(n_S = 1.6\) for the UCL018 film. The PL efficiency of Coumarin 6 is \(\eta_{PL} = 78\%\) and the EQE of the solar cell combined with the in-coupling is simulated to be 85\%. The thickness of the PMMA and UCL018 films were adjusted to result in an absorption of 42\% in the films, identical to experimental conditions. To match our experimental procedures, the input light is defined monochromatically at normal incidence for both \(s\) and \(p\) polarizations. For these simulations an input photon count of 30,000 was used that resulted in uncertainties of less than \(\pm 0.5\%\).

We simulate EQE as a function of \(G\) for two different experimental configurations. The first configuration simulates the spot excitation technique and calculates the number of photons coupled to one of the edges as a function of the distance between that edge and the spot excitation. The correction factor presented above is then used to account for the different angle subtended by the solar cell at each spot distance, and multiplying by the EQE of the solar cell attached to the edge yields the EQE of the LSC. The second configuration simulates EQE versus \(G\) for a uniformly illuminated LSC. The fraction of photons coupled to the four edges is multiplied by the EQE of the GaAs solar cell to obtain the EQE of the LSC.

3.5 Experimental Results

3.5.1 Measured trapping efficiency

Figures 3-7(a) and 3-7(b) summarize the trapping efficiency for isotropic and vertically-aligned LSCs, respectively. The total absorption within both samples is 40%. One can observe a clear enhancement of the edge emission for the vertically aligned LSC over the isotropic LSC. To allow for a more quantitative assessment of the enhancement in edge emission, Fig. 3-7(c) presents the trapping efficiency for both the isotropic and the homeotropic LSCs. The trapping efficiency of the vertically aligned LSC is measured to be 81%, while the isotropic dye system results in a trapping efficiency of 66%. To the best of our knowledge, the vertically-aligned device exhibits the highest measured LSC trapping efficiency to date, although we note that the trapping efficiency of LSCs with dielectric mirrors has not been explicitly reported [20]. Comparing these measured trapping efficiencies to theoretical predictions for \( \eta_{\text{trap}} \) presented in Fig. 3-4(b), however, shows that the measured trapping efficiency of the vertically aligned and the isotropic LSC is lower than theoretically predicted. We demonstrate below that this is due, at least in part, to imperfect vertical alignment.

3.5.2 Absorption as a function of the incident angle

Next, we measure optical absorption as a function of the incident angle of the excitation beam for vertically aligned LSCs and isotropic LSCs. Increasing the coupling of radiation into the waveguide by aligning the transition dipole moment of the dyes perpendicular of the waveguide is expected to come at the expense of a reduced capability to absorb perpendicularly incident radiation.

Figure 3-8(a) presents the power emitted from the edge of the vertically aligned LSC and the isotropic LSC as a function of incidence angle, \( \theta \). The measured power is normalized to the edge emission at normal incidence. We correct for the
Figure 3-7: The measured Optical Quantum Efficiency (OQE) of the facial emission (blue dots), edge emission (green dots) and the total emission (red dots) of (a) the isotropic LSCs, and (b) the vertically aligned LSCs. Both samples absorb 40% of the incoming light. (c) The measured trapping efficiency, $\eta_{\text{trap}}$, of the isotropically aligned LSCs (red dots) and the vertically aligned, homeotropic, LSCs (green dots). This measured $\eta_{\text{trap}}$ is the ratio between the edge and the total emission OQEs.

The expected increase in pump absorption at higher incidence resulting from the increased path length in the film by multiplying the measured edge power by a factor $(1 - \exp(-\alpha t))/(1 - \exp(-\alpha t/\cos(\theta_I)))$, with $\theta_I$ being the internal angle in the film (assuming $n_s = 1.5$ for PMMA and $n_s = 1.6$ for UCL018), $\alpha$ is the absorption coefficient and $t$ is the thickness of the film. The product $\alpha t$ is determined from the absorption at normal incidence. The change in reflection off the face of the sample with increasing incident angle is calculated to be $\sim 2\%$ and is neglected. The performance of the isotropic sample is approximately constant with excitation angle, while the performance of the homeotropically aligned LSC increases monotonically. This is consistent with an increased ability of the vertically aligned dipoles to absorb light at higher angles, whereas the trapping efficiency of isotropic dipoles is only weakly dependent on the incident angle of the excitation light (see Eqs. 3.5 and 3.6).

We also plot theoretical expectations for the increase in edge emission resulting from an enhancement in trapping efficiency with increasing excitation angle for an isotropic and vertically aligned LSC (dashed red and green lines respectively). The
trapping efficiency is constant over all excitation angles for an LSC employing perfectly aligned vertical dipoles. An increase in edge emission would therefore follow the \( \sin^2 \theta \) behavior of the absorption in the film. We normalize the theoretical prediction of the edge power to the measured edge power at 45\(^\circ\). The fact that the absorption of the vertically aligned LSC deviates from the behavior of a perfectly aligned homeotropic system suggests that the actual alignment in the film is not ideal, partly explaining the lower value for the measured trapping efficiency than the theoretical models predict.

![Graph showing normalized edge power as a function of excitation beam angle and diffusing angle.](image)

Figure 3-8: (a) The power emitted from the edge of an LSC as a function of the incoming angle of the excitation beam for a isotropic LSC and a vertically aligned LSC. The edge power is normalized to the power at normal incidence. The monotonic increase in performance of the vertically aligned LSC is consistent with an increased ability of the vertical dipoles to absorb light at higher angles. The theoretical predictions for the edge emission versus incident angle are plotted as a dotted line. (b) Effect of an external diffuser on the edge output power of an isotropic (red dots) and homeotropic LSC (green dots). Increasing the diffuser strength improved the performance of the vertically aligned LSC, while the isotropic LSC hardly benefits.

**External diffusers for enhanced absorption** To alleviate the weak absorption of homeotropically aligned LSCs under perpendicularly-incident light, we employ external holographic diffusers. The edge power of the LSC is monitored as a function of
diffuser strength and is presented in Fig. 3-8(b). The edge power is normalized to the edge power measured without the presence of the diffuser. The initial drop in edge-power at a diffuser strength of $10^\circ$ results from the non-unity transmission efficiency of the diffuser. The vertically aligned, homeotropic LSC shows a clear improvement with increasing diffuser strength. The edge emission for the system that included the $60^\circ$ diffuser is $10\%$ better than the system without diffuser, and $20\%$ better than the LSC result for the $10^\circ$ diffuser. As expected, the isotropic LSC does not show an overall enhancement in performance due to the presence of the diffusers.

3.5.3 The performance versus optical concentration

In Fig. 3-9, we plot the external quantum efficiency for vertically-aligned and isotropic LSCs as a function of $G$. Consistent with an enhanced trapping efficiency of the homeotropic, vertically aligned LSCs, their performance is approximately $16\%$ better than the isotropic LSCs for all measured concentration factors. We also simulate the performance of the isotropic and homeotropic LSCs as a function of concentration factor. To test the accuracy of the spot excitation-technique, we simulated both spot-illuminated waveguides (open squares) and uniformly illuminated waveguides (open circles) of various sizes. The Monte Carlo simulations closely resemble the experimentally obtained results demonstrating that the spot illumination technique accurately represents the concentration dependence of quantum efficiency, at least for these LSC samples.

3.6 Discussion and Conclusions

We have enhanced the overall performance of LSCs by $16\%$ by aligning the dipole moment of dye molecules perpendicularly to the waveguide. We have also demonstrated that an external diffusing medium can help alleviate reduced absorption of incident
Figure 3-9: (left axis) The external quantum efficiency (EQE) versus geometric gain for vertically aligned LSCs (red dots) and isotropic dipoles (green dots). Both samples absorbed 42% of the incoming radiation. Monte Carlo simulations for uniformly illuminated LSCs (open circles) and simulations of the spot excitation technique (open squares) yield slightly higher results due to the higher trapping efficiency obtained in the Monte Carlo simulations compared to measured trapping efficiencies. (right axis) The measured ratio of the EQE of the vertically aligned LCS is 16% higher than the isotropic standard for all measured geometric gains, consistent with the higher measured trapping efficiency.

sunlight by vertically aligned dipoles. The improvement is due to an increase in trapping efficiency. We measure \( \eta_{\text{trap}} = 81\% \) for an LSC employing vertically aligned dye molecules compared to \( \eta_{\text{trap}} = 66\% \) for an LSC based on randomly oriented dye molecules. The increase is consistent with theory that models the system using Hertzian dipoles embedded in a waveguide. This theory also predicts small but significant changes to the commonly-cited trapping efficiency of LSCs employing isotropic dipoles. For example, the trapping efficiency of a waveguide of \( n = 1.5 \) under normally incident light is \( \sim 71\% \) as compared to 74.5% under the standard analysis.

Finally, dye alignment is not the only means of enhancing the trapping efficiency of LSCs. It is also possible to increase the trapping efficiency by employing wavelength selective mirrors [20, 64, 65] or high refractive index waveguides. But dielectric
mirrors require many layers to achieve omni-directional reflectivity at the luminescent wavelengths and high transmission for the broadband solar excitation at all incident angles. The fabrication of such mirrors may prove costly. Materials with high refractive indices are also typically more costly than conventional glasses and plastics. Consequently, aligning the transition dipoles of dye molecules perpendicular to the waveguide may be the most promising path to higher efficiency LSCs.
Chapter 4

Dye Alignment in Luminescent Solar Concentrators: II. Horizontal Alignment for Energy Harvesting in Displays

This chapter introduces a new strategy for harvesting energy in display applications using Linearly Polarized Luminescent Solar Concentrators (LP-LSCs).

4.1 Motivation for energy harvesting in displays

Displays are an interesting candidate for energy harvesting. Firstly, their areas are ever increasing; flat panel television screens commonly exceed several square feet in area (see Fig. 4-1(a)); video displays already cover nearly the full surface area of lap-top computers and DVD players and are occupying ever greater fractions of the surface area of cell phones and music players. Examples of the latter trend include Apples iPhones and iPods, whose the display occupy almost the entire front surface
Figure 4-1: Displays are interesting candidates for energy harvesting applications. (a) Displays make up significant portions of the surface area of cell phones and music players. A strategy that can simultaneously use this area for energy harvesting can help to extend battery life. (b) The area of displays is ever increasing, as exemplified by Mitsubishi Electric’s 155-inch sized OLED display, which was displayed during the Ceatec 2009. From [66].

of the device (see Fig. 4-1(b)). Secondly, displays are the chief consumers of power in portable electronics. Hence, effective energy scavenging strategies could significantly extend battery life. Thirdly, displays in fact naturally collect light; emissive displays must absorb all incident light in order to maximize the contrast ratio and image quality. Linear polarizers play a crucial role by selectively absorbing one polarization component of the incident light.

Linear polarizers are typically composed of stretched poly(vinyl–alcohol) films doped with iodine crystals or dichroic, black, organic dyes. See Fig. 4-2(a) for the absorption of light polarized parallel (blue line) and perpendicular (red line) to the absorptive axis of the polarizer. They are specifically crucial to liquid crystal displays, but linear polarizers are generally useful for improving contrast ratios in many display technologies. Combined into a circular polarizer, linear polarizers absorb 50% of light incident on a display and ideally, the remaining incident light is absorbed when its polarization reverses rotation upon any reflection from within the display; see Fig.
Figure 4-2: (a) The absorption of a polarizer sheet for light whose electric field is parallel (blue line) or perpendicular (red line) to the absorptive axis of the polarizer. (b) The working of a LCD pixel. When the pixel is in its "on" state, light enters through the front of the LCD and passes through the first vertical linear polarizer. The liquid crystal layer rotates the polarization by 90°, after which the light passes the second horizontal polarizer. The light then hits the mirror bounces right out the same way it came in. But when a current is supplied to the electrodes, the liquid crystals between the electrodes untwist and does not rotate the polarized light by 90° when it passes through. As a result, all the vertically aligned light is absorbed in the 2nd horizontal polarizer. This makes the pixel appear black. Picture taken from [67].

Incidentally, polarizers also absorb at least 50% of the displays own light. All this energy is wasted as heat.

4.2 Strategy and device layout

Here, we describe linear polarizers that do not waste the absorbed light as heat, but rather act as luminescent concentrators [13, 14, 15, 16, 17, 18, 19, 20]. Such linearly-polarized luminescent solar concentrators (LP-LSCs) are a promising approach to light harvesting in portable devices with flat panel displays. LP-LSCs can replace or be used in combination with the linear polarizers present in existing display technologies, redirecting previously wasted light to solar cells mounted in the frame of
the display. They allow for energy harvesting over the full surface of the display with minimal image distortion or reduction in display brightness.

Previous work on energy harvesting in displays has investigated the integration of solar cells within organic light emitting device (OLED)-based displays [68, 69]. But the wide bandgap III-V based solar cells best suited for indoor light harvesting are relatively expensive [19]. In addition, solar cells must be positioned behind the displays light source, and consequently, the solar cells are shadowed by the driving electronics in the backplane. Finally, the efficiency of solar cells decreases markedly under the low light levels typical of indoor applications[70].

Figure 4-3: A schematic representation of a Linearly Polarized Luminescent Solar Concentrator (LP-LSC) for energy harvesting in displays. Most displays employ purely absorptive linear polarizers to improve their contrast ratio. In this linearly polarized LSC, dichroic dye molecules are aligned in the plane of a thin, flat plate waveguide using a polymerized liquid crystal host or a stretched polymer as a scaffold. The absorption of the waveguide is linearly polarized ambient light or light from the back-plane is absorbed very strongly for polarizations parallel to the dipole moment of the dye molecules. However, perpendicular polarized light is transmitted, leaving the entire front surface of the device available for the display.

Conventional LSCs employ randomly oriented luminescent dye molecules that are embedded in a transparent waveguide. The dyes absorb diffuse light incident on the waveguide, and re-emit these photons isotropically at a lower energy [5]. A fraction
of the re-emitted photons are trapped within the waveguide through total internal reflection — identical to the operational principle of an optical fiber. These trapped photons are funneled to the edges of the concentrator where photovoltaic elements are placed to collect the photons and convert them to electrical energy. When the area of the face of the waveguide is larger than the area of the edges, the light can be concentrated, an important attribute for efficient energy harvesting under low light conditions [70].

Unlike conventional LSCs, Linearly Polarized Luminescent Solar Concentrators (LP-LSCs) have aligned dye molecules; see Figure 4-3. They have been demonstrated previously with the aim of selectively coupling incident light to solar cells mounted perpendicularly to the polarized axis of an LSC, thereby improving the geometric gain of the LSC at the cost of poor absorption off axis [71].

Here, we consider LP-LSCs as replacements for conventional linear polarizers in energy harvesting applications. As in Chapter 3, we employ dichroic dye molecules linearly aligned in the plane of the substrate [71]. LP-LSCs preferentially absorb light for which the electric field is parallel to the dipole moment of the dye molecules, causing the optical transmission of the LP-LSC to be linearly polarized, just like in an ordinary polarizer. However, instead of dissipating the absorbed photons as heat, a linearly polarized LSC will funnel the captured photons to photovoltaic elements placed at the edges of the waveguide (see Figure 4-3). Hence, this concept allows the photovoltaics to be located in the frame of the display, which minimizes their area, while leaving the entire front surface available for the display.

As a proof of concept, we create and characterize a LP-LSC based on the rod shaped dye molecule, Coumarin 6 (3-(2-Benzothiazoly)-N,N-diethylumbelliferylamine), within a polymerizable nematic liquid crystal identical to a typical guest host system [72, 73]. Ultimately, to improve the harvesting of indoor radiation across the visible spectrum, it may be preferable to create a linearly polarized LSC that hosts several
dye molecules that cascade in energy. For this purpose we also create and characterize a LP-LSC that employs two dye molecules, 4-dicyanomethyl-6-dimethylaminostiryl-4H-pyran (DCM) and Coumarin 6.

4.3 Linearly Polarized LSC Fabrication

The LP-LSCs are created on a 1-mm-thick glass substrate with a refractive index, $n_S = 1.7$ (SF10, Schott). The glass substrates are cut with a dicing saw to obtain the desired dimension. The geometric gain of a LSC, $G$, is defined as the ratio of the face area versus PV area and is given by $G = \left(\frac{L}{4d}\right)$, where $L$ is the length of the LSC and $d$ is the thickness (assuming PV elements are placed on all four edges of a square collector). For measurements of optical quantum efficiency (the fraction of photons coupled to the edges of the LSC), the glass substrates are cut to squares of $2 \times 2$ cm, while for measurements of the external quantum efficiency (the fraction of incident photons converted to current in solar cells) the substrates are cut to a substrate size of $7.6 \times 9.5$ cm. The glass is thoroughly cleaned with a detergent solution, DI water and solvents.

To create the alignment layer, a polyimide acid (SE410, Nissan Chemical Industries, LTD) is diluted to a ratio $1:1$ with Solvent 25 (Nissan Chemical Industries, LTD), and spin-cast on the clean substrates in air with a ramp of $1000$ rpm/sec and a spin speed of $2500$ rpm for 30s. Subsequently, the samples are baked on a hotplate in still air for $10$ min at $80^\circ$C and $60$ minutes at $180^\circ$C. The coated samples are hand-rubbed with a velvet cloth to introduce alignment in the liquid crystal layer. The polymerizable nematic liquid crystal host chosen for in this study is Paliocolor 242 (BASF) (see Fig. 4-4 for the chemical structure). The dyes used for the experiments are Coumarin 6 and DCM (both purchased from Sigma Aldrich). Their structures are also given in Fig. 4-4. We selected these dyes because they are known to possess a
Figure 4-4: Chemical structures of the materials used for the linearly polarized LSC studies. The liquid crystal host material used is Paliocolor LC242. The dichroic dye molecules are 4-dicyanomethyl-6-dimethylaminostiryl-4H-pyran (DCM) and 3-(2-Benzothiazolyl)-N,N-diethylumbelliferylamine (Coumarin 6).

relatively high dichroic ratio [58] and their photoluminescence efficiency is reasonably high (measured to be 78% and 60%, respectively). Coumarin 6 also possesses a large Stokes shift, which makes this dye especially suitable in an LSC [19, 59, 29]. Some of our experiments are performed with Coumarin 6 as the sole dopant (at a 1% solid weight content), while a second set of experiments contains both Coumarin 6 and DCM (both dyes at a 1% solid weight content).

In the following procedure all percentages of the separate components are given in weights relative to the total weight of the mixture. In a vial, a solution is prepared that contained Paliocolor (30%), Coumarin 6 (0.30%) or both DCM and Coumarin 6 (both at 0.30%). To these powders, toluene is added (68.95%) and gently stirred. As a surfactant BYK-361 (BYK-Chemie) is used (0.15%), which is taken from a pre-prepared solution of 5% BYK-361 dissolved in toluene. Lastly, Irgacure 184 (0.60%, Ciba Chemicals) is added as a photo initiator. When the components are well dissolved the solution is spin-cast on the pre-rubbed substrates. The samples are dried for 3 minutes at room temperature in still air, after which they are placed for 4 minutes on a hotplate at 80°C (also in still air). The samples are cooled down to room temperature for 1 minute before placing them under a UV lamp (365 nm) for 3 minutes to cure. This spin speed is adopted to yield a film thickness that results in a
peak absorption of 78% for light that is polarized parallel to the rubbing direction for the Coumarin 6 LP-LSCs. This film-thickness is estimated to be 1.1 microns thick through optical modeling. All thin film absorption measurements are obtained using an Aquila spectrophotometer.

4.4 Experimental LP-LSC Device Characterization

4.4.1 Absorption and photoluminescence

![Absorption and photoluminescence](image)

Figure 4-5: Polarized absorption and photoluminescence of the linearly polarized LSCs used in this study. The absorption of light polarized parallel to the rubbing direction is depicted as a solid red line, and the blue dotted line is light polarized perpendicular to the rubbing direction. The photoluminescence is plotted as a dotted green line. The left panel depicts the absorption of liquid crystal host doped with 1% C6 (solid weight content), while the right panel shows the results for a sample co-doped with C6 and DCM (both at 1% solid weight content).

The absorption and photoluminescence spectra of the LP-LSCs are presented in Fig. 4-5. The absorption is measured both parallel (solid red line) and perpendicular to the rubbing direction (dotted blue line). From these measurements the order parameter, \( S \), defined by \( S = (A_\parallel - A_\perp)/(A_\parallel + 2A_\perp) \) [74], is determined. Here, \( A_\parallel \) is defined as the absorbance of the sample for incident light polarized parallel to the rubbing direction, and \( A_\perp \) is the absorbance for light polarized perpendicular to the
rubbing direction. The samples that contained solely Coumarin 6 are found to have an order parameter of 0.52, while the samples that contained both Coumarin 6 and DCM are measured to have an order parameter of 0.45. These ratios are not ideal for commercial applications, but serve instead as a proof of principle. The absorption of the C6-DCM sample is extended relative to the C6 sample but still exhibits dichroism. Optimized dye systems are expected to have considerably better order parameters, but this is outside of the scope of this work.

The photoluminescence (PL) spectra of the C6 and DCM-C6 sample are plotted as dotted green lines in Fig. 4-5. These spectra are obtained from the face of the device under excitation by a $\lambda = 408$ nm laser. The photoluminescence efficiency of the C6 samples is measured with an integrating sphere and found to be 78%, close to literature values [57]. The luminescence of the C6-DCM sample originates from the DCM dyes, confirming that energy is effectively funneled to the DCM molecules through Förster transfer [19, 36]. The PL efficiency of the C6-DCM samples is measured to be 60%, also in close agreement with literature [75]. The similarity between literature and measured PL efficiencies suggests that the dyes are not quenched nor degraded during our device fabrication procedure.

4.4.2 The optical quantum efficiency spectra

The optical quantum efficiency, OQE, defined as the fraction of photons coupled to the edges of the LSC, is a key performance parameter. It is characterized within an integrating sphere (see Fig. 2.3.2 for a schematic representation of the set-up). We discriminate between edge and facial LSC emission by selectively blocking the edge emission with a black marker, which has been tested to block above 98% of the internal reflection. The OQE is determined for light that is polarized parallel and perpendicular to the rubbing direction, i.e. polarized along the long or short axis of the dye molecules. These spectrally resolved measurements use a 150W Xenon lamp
Figure 4-6: The OQE for a linearly polarized LSC based on Coumarin 6 dye molecules (left panel) and a sample co-doped with Coumarin 6 and DCM.

that is coupled into a monochromator and chopped at 73 Hz. The photoluminescence for the OQE measurements is detected by a Si photodetector mounted directly on the integrating sphere and which in turn is connected to a lock-in amplifier.

The spectrally resolved OQE of the C6 and the C6-DCM samples is shown in Fig.4-6. The samples used for these measurements are identical to the samples used for the absorption measurements presented in Fig. 4-5. The C6 sample has a peak OQE of 38% for light that is polarized parallel to the rubbing direction (red dotted line). This efficiency number is the product of the peak absorption of 78% for this polarization (see Fig. 4-5), a PL efficiency of 78% and a trapping efficiency of 62%. The trapping efficiency is determined within the integrating sphere and discussed in our companion paper [76]. For light that is polarized perpendicular to the rubbing direction (dotted green line) the maximum OQE is measured to be 17%. This lower number results from the lower absorption (33%) within the sample for this polarization (See Fig. 4-5). The sample that contains both C6 and DCM has a peak OQE of 34% for light that is polarized parallel to the rubbing direction, as can be seen in the right panel of Fig. 4-6. This number is the product of an absorption of 93% (Fig. 4-5 right panel), a
measured photoluminescent efficiency of 60%, and a trapping efficiency of 62%. The perpendicular polarization results in a peak OQE of 18% (dotted green line). When unpolarized light is used as an excitation source the OQE is measured to be 25%, a perfect average of the OQEs measured for the parallel and perpendicular polarized excitation sources (dotted blue line).

4.4.3 The external quantum efficiency versus optical concentration

Figure 4-7: (a) The performance of linearly polarized LSCs based on Coumarin 6 dye molecules as a function of geometric gain is simulated by measuring the current coming out of a solar cell attached to the edge of the LSC while varying the distance, \(d\), between the excitation spot and the solar cell. This measurement is performed on LP-LSCs for which the dye molecules are aligned parallel (left schematic) or perpendicular (right schematic) to the solar cell. (b) The external quantum efficiency versus geometric gain, \(G\), of the LP-LSCs. The performance of the parallel dipole LSC drops off faster than the LP-LSC for which the dipoles are aligned perpendicular to the solar cell. This is the result of the larger self-absorption of the first geometry, since there is a larger overlap between the emissive dipole and the absorptive dipole or these photons travelling towards the solar cell. The blue curve represents the performance of a uniformly illuminated LSC and is the weighted average of the two curves.
Next, we examine the performance of the LP-LSCs as a function of concentration factor, $G$, which we defined above as the ratio of the facial area to the PV area (assuming PV elements are placed on all four edges). A GaAs solar cell from Spectrolab with an external quantum efficiency (electrons out per photon in) at the emission wavelength of Coumarin 6 of 85% is cut into 3.8 cm × 0.34 cm strips. Two of these cells are connected in series, and attached to one of the short edges of the concentrator with index matching fluid (Norland Products) (see Fig. 4-7(a)). The other 3 edges are blackened out with a black marker to prevent indirect luminescence from reaching the solar cell. We test the performance of the external quantum efficiency for LP-LSCs based on Coumarin 6 for which the dipoles are aligned parallel or perpendicular to the solar cell (see Fig. 4-7(a)).

Concentration factor-dependent measurements are obtained by directing an excitation beam perpendicular to the LP-LSC so as to create an excitation spot of $\sim 1 \text{ mm}^2$, while the distance, $d$, between the spot and the solar cell is varied; see Fig. 4-7(a). This is an experimentally convenient technique to simulate the performance of a uniformly-illuminated LP-LSCs that collects power from all four edges at different geometric gains. This experimental technique provides a lower bound for performance since the average path-length is slightly longer than a uniformly illuminated LSC [76]. The measured photocurrent is divided by a geometric factor that corrects for the fraction of the total trapped power emitted by a dipole within an angle subtended by the solar cell at each illumination spot position, $d$; see Fig. 4-7(a). This geometric correction factor must also account for non-isotropic emission from the aligned dipoles. Following the approach for calculating the time-averaged power density of a Hertzian dipole as outlined in our accompanying paper [76], two different correction factors are derived for a dipole that is either oriented parallel (in the $\hat{y}$ direction) or perpendicular (in the $\hat{x}$ direction) to the solar cell. Integrating the expression for the power density distribution of a dipole oriented along the $y$-axis
over the solid angle from $-\phi'$ to $\phi'$ and from $\theta_C$ to $\pi - \theta_C$, where $\theta_C$ is the critical angle and subsequently normalizing by the total power emitted by the dipole which is trapped in the waveguide, yields the following expression for the correction factor for the parallel dipole, $f_\parallel$:

$$f_\parallel = \frac{\cos^3 \theta_C \left[ \phi' - \frac{1}{2} \sin 2\phi' \right] + 2 \cos \theta_C \left[ \phi' + \frac{1}{2} \sin 2\phi' \right]}{\left[ \frac{2}{3} \cos^3 \theta_C + 2 \cos \theta_C \right] \cdot \pi}$$  \hspace{1cm} (4.1)

Similarly, we obtain the following correction factor for dipoles oriented perpendicular to the solar cells, $f_\perp$:

$$f_\perp = \frac{\cos^3 \theta_C \left[ \phi' + \frac{1}{2} \sin 2\phi' \right] + 2 \cos \theta_C \left[ \phi' - \frac{1}{2} \sin 2\phi' \right]}{\left[ \frac{2}{3} \cos^3 \theta_C + 2 \cos \theta_C \right] \cdot \pi}$$  \hspace{1cm} (4.2)

Here, $\phi' = \tan^{-1}(L/2d)$. The external quantum efficiency (EQE) as a function of geometric gain, $G$, for the LP-LSCs is presented in Fig. 4-7(b). The results obtained for dipoles that are aligned parallel to the solar cell are depicted as a red dotted line, while the perpendicular dipoles are presented as green dots. The EQE is measured at $\lambda = 465$ nm.

It is observed that the parallel dipoles have a more pronounced roll-off in efficiency with increasing concentration factor, resulting from stronger overlap between the emissive and absorptive dipoles along the path that the photons have to travel towards the solar cell. A uniformly illuminated LP-LSC will have a performance that is the average of the two curves weighted by $f_\parallel$ and $f_\perp$, each evaluated at $\phi = 45^\circ$ (blue line in Fig. 4-7(b)). The theory yields a ratio of emission to the edges parallel and perpendicular to the dipoles of 2.4:1, respectively. Due to stronger self-absorption for light coupled to the parallel edges, the measured ratio is 2:1.
4.5 Extending the absorption of LP-LSCs over the full visible spectrum

For LP-LSCs to be commercially interesting, the absorption of the LP-LSC will need to be extended over the full visible spectrum, while shifting the emission of the emitting (lowest energy) dye into the infra-red [77]. For this purpose, we manufactured a LP-LSC incorporating five different dichroic dye molecules with cascading energy: Coumarin 6, DCM, Nile Red (9-diethylamino-5-benzo[a]phenoxazinone), Pyrromethene 650 (1,2,3,5,6,7-hexamethyl-8-cyanopyrromethene-difluoroborate complex) (PM650) and a custom-synthesized squaraine dye (1,3-Bis[4-(dioctylamino)-2-hydroxyphenyl]-2,4-dihydroxycyclobutenediylium dihydroxide, bis(inner salt)). The chemical structures of the dyes are given in Fig. 4-8. The nematic liquid crystal MLC-2091 (Merck) was used as a host material. The precise chemical structure of this liquid crystal is proprietary information.

The LP-LSCs were prepared as follows. First, the five dyes were dissolved in chloroform and subsequently mixed with the liquid crystal host. The dye concentrations (in weight % with respect to the liquid crystal host) were 0.3% for C6, 0.3% for DCM, 0.6% for Nile Red, 0.8% PM650 and 0.2% for the squaraine dye. The final solution was kept at 60°C on a hot-plate for five minutes while stirring the solution before evaporating the solvent over a period of twelve hours in a desiccator.

The liquid crystal host and dye molecules were aligned in the plane of the waveguide using liquid crystal testing cells from Instec that incorporate an anti-parallel alignment layer. Experiments were performed on cells with a gap of 5 μm. A small amount of the liquid crystal and dye mixture was placed in front of one opening of the empty cell. Capillary forces dragged the mixture into the cell. To speed up the filling process, all the materials were heated to 70°C, which is above the isotropic phase transition temperature of the liquid crystal. After a couple of minutes, the cell
Figure 4-8: Chemical structures of the 5 dyes used for the linearly polarized LSC with extended absorption. The dichroic dye molecules are 4-dicyanomethyl-6-dimethylaminostiryl-4H-pyran (DCM), 3-(2-Benzothiazolyl)-N,N-diethylumbelliferylamine (Coumarin 6), 9-diethylamino-5-benzo[a]phenoxazinone (Nile Red), 1,2,3,5,6,7-hexamethyl-8-cyanopyrromethene-difluoroborate complex (Pyrromethene 650) and 1,3-Bis[4-(dioctylamino)-2-hydroxyphenyl]-2,4-dihydroxycyclobutenediylium dihydroxide, bis(inner salt) (squaraine).

had filled and it was then cooled down slowly to room temperature to assure good alignment.

Figure 4-9 presents polarized absorption and photoluminescence spectra of the resulting LP-LSCs. The absorption of light polarized parallel to the rubbing direction and polarized perpendicular to it are each plotted, as is the photoluminescence, which was obtained by exciting the sample with a 408 nm laser while collecting emission from the face. As can be observed in Figure 4-9, the combined absorption of these five dyes spans almost the whole visible spectrum (from 350 nm until 650 nm), while photoluminescence is shifted towards $\lambda = 670$ nm.

The operation of this LP-LSC as a polarizer is demonstrated in Fig. 4-10. There, we present two photographs of a computer screen in front of which a LP-LSC was placed. As discussed in Section 4.1, the emission of a display is linearly polarized. In Figure 4-10(a) the absorptive axis of the LP-LSC is aligned parallel to the display
Figure 4-9: Polarized absorption and photoluminescence of the linearly polarized LSCs that has an extended absorption over the full visible spectrum. This LP-LSC contains five different dye molecules that are doped into a liquid crystal host. The absorption of light polarized parallel to the rubbing direction is depicted as a blue line, and the red line is light polarized perpendicular to the rubbing direction. The photoluminescence is plotted as a green line.

emission polarization, whereas in Fig. 4-10(b) we rotated the sample by 90° and the absorptive axis is perpendicular to the display emission polarization. Note that the light from the Dutch sky that is transmitted in Fig. 4-10(a) becomes almost completely absorbed within the LP-LSC in Fig. 4-10(b).

4.6 Conclusions and Outlook

To conclude, we propose that Linearly Polarized Luminescent Solar Concentrators (LP-LSCs) may replace conventional linear polarizers when energy harvesting is desired. Previous studies have suggested that indoor light harvesting using solar cells can generate in excess of 10 μW/cm² under typical office lighting conditions (400 lux) [70]. LP-LSCs should be able to generate similar or higher power densities be-
Figure 4-10: Photograph of a LP-LSC in front of a computer screen. The absorptive axis of the LP-LSC in (a) is aligned parallel to the display emission polarization, and (b) perpendicular to the display emission polarization.

cause they concentrate light, which is an advantage for photovoltaic conversion under low light intensity [70]. In addition, they can exploit the full surface area of a display. The technology can be integrated within displays with two modifications to display functionality: there will be some luminescence emitted through the face of the display, and the LP-LSC must be optically isolated to permit optical waveguiding. Although not fully pursued here, the use of infrared dyes is a promising solution to the first concern, and low index cladding layers may be necessary to prevent facial scattering of guided radiation at LP-LSC surfaces. Future work must also improve the order parameter and extend the wavelength coverage of LP-LSCs even further into the infrared to enable energy harvesting across the full visible spectrum. Aligned luminescent polymers and energy transfer from aligned hosts to isotropic guests offer two promising research directions. But the development of efficient dichroic near infrared dye molecules is especially desirable because infrared dye molecules can capture the red portion of the visible spectrum and infrared emission will minimize image distortion due to radiation escaping from the face of the waveguide.
Chapter 5

The Contribution of Waveguiding and Self-absorption to the Transport of Triplet Excitons in Tetracene and Rubrene Crystals

Luminescent Solar Concentrators use optical waveguiding to transport photons to solar cells. This chapter discusses the contribution of waveguiding and self-absorption to the transport of triplet excitons in tetracene and rubrene crystals.

5.1 Introduction

Exciton transport plays a vital role in organic photovoltaics because it delivers excitons from a photon-absorbing molecule to a charge transfer site in organic solar cells.[78, 79, 80, 81]. The long lifetimes of triplet excitons (total spin 1) relative to singlets (total spin 0) [33] make the former interesting candidates for extending the practical distance between the absorption of a photon and charge separation [79, 33].
Indeed, the diffusion length of triplets in rubrene crystals was recently reported to be 2-8 μm, [82, 83] exceeding reported triplet diffusion lengths in thin film materials by two orders of magnitude [80, 84].

However, triplet diffusion lengths have so far been inferred from indirect measurements and analyses that presumed an exclusively diffuse transport mechanism. Na-jafov et al. used polarization- and wavelength-dependent photoconductivity measurements to obtain diffusion lengths of triplet excitons of 2-8 μm in rubrene crystals[83]. Aladékomo et al. measured a triplet diffusion length of ~ 6 μm in tetracene crystals along the crystal b axis by examining the decrease in delayed fluorescence at localized sites where excitons were initially created with a periodic grating [85]. Recently, Irkhin et al. reported a triplet diffusion length of ~ 4 μm in rubrene crystals by measuring the spatial exponential decay of photoluminescence from a localized excitation spot [82]. These previous studies did not consider the possibility that energy could be transported by self-absorption and re-emission, a mechanism whereby singlet excitons emit a photon that becomes waveguided some distance by the host material before being re-absorbed to create another singlet exciton. An early review of singlet exciton transport in organic crystals by Soos and Powell already warned for the effect of radiative re-absorption on different types of experiments to determine the singlet exciton-transfer parameters such as the singlet diffusion length [86]. The mechanism's potential importance needs to be reconsidered in the context of recent studies of triplet transport in organic crystals like tetracene and rubrene where singlets and triplets can interconvert through fission and fusion.

Overview Here, we report clear experimental and theoretical evidence that the transport of triplet excitons in rubrene and tetracene crystals is dominated by self-absorption and waveguiding in the regime of high exciton density commonly found in experiments measuring triplet diffusion. We create triplet excitons via fission of
Figure 5-1: We study the time- and spatially resolved distribution of photoluminescence in tetracene and rubrene crystals with an imaging set-up. Singlet excitons are created with a focused pulsed laser beam. From the observation of strong photoluminescence at long time-scales (several micro-seconds) with our CCD-camera, we infer that triplets are formed by singlet fission (black arrows). The observed spreading of the luminescence patterns with time can result of 2 distinct transport mechanisms: (a) Triplets created by fission diffuse over a distance $L_d$ before colliding with another triplet exciton forming a secondary singlet exciton, whose subsequent decay we can optically detect with a CCD-camera; or (b) The initial singlet emits a photon that is waveguided and self-absorbed after a distance $L_a$, creating a secondary singlet, which can relax while re-emitting a photon. The actual transport of triplets in crystalline tetracene and rubrene is likely a combination of these 2 distinct transport mechanisms.

singlet photoexcitations [87] and study the time- and spatially resolved triplet distribution by monitoring delayed fluorescence. Delayed fluorescence results when two triplets combine to create a singlet exciton (see Fig. 5-1(a) for a schematic representation of the process). Our technique allows us to directly image the transport of triplets in the a, b and c crystallographic directions of crystalline tetracene and rubrene with sub-micrometer resolution. Contrary to expectations for triplet diffusion, the delayed fluorescence from a locally excited spot expands equally along every crystallographic axis and to an extent that depends on the intensity of the excitation. The waveguiding and self-absorption mechanism explains these findings (see Figure 5-1(b) for a schematic representation of this transport mechanism). Furthermore, simulations of the triplet distribution as a function of time and pump intensity
support this interpretation. These results underscore the importance of accounting for self-absorption and waveguiding in measurements of exciton transport in organic crystals. The mechanism is likely to become critical to understanding and optimizing the efficiency of organic photovoltaics and possibly other optoelectronic devices.

5.2 Experimental methods

![Schematic representation of the crystal growth system.](image)

Figure 5-2: Schematic representation of the crystal growth system. The organic material sublimes at a temperature of $T_1$ and is transported to a cooler region of the tube by the carrier gas where it recrystallizes at a temperature $T_2$. Light impurities with higher volatility than the pure compound will condense at a lower temperature $T_3$, which corresponds to another position in the tube. Heavy impurities with a lower volatility will be left behind at the position of the source material. This might lead to a purification of the material.

We studied single crystals of tetracene and rubrene grown from 99.99% pure tetracene and rubrene source materials (Sigma-Aldrich), transported in the vapor phase using and ultra-pure argon carrier gas (see Fig. 5-2 for a schematic and Fig. 5-3(a) for a picture of the crystal growth set-up) [88]. Crystal thicknesses varied from 1 $\mu$m to tens of $\mu$m (see Fig. 5-3(b)), while the crystals were elongated in the ab-plane, with dimensions in the millimeter range. The highly asymmetric crystal dimensions resulted from the different growth rates along the three crystal axes, which are illustrated in Fig. 5-4(a) and (b). The crystal axes are easy to identify, and we made use of this fact to study the transport of excitonic energy along different crystallographic
Figure 5-3: (a) Photograph of the organic single crystal growth system. Arrows indicate the location of the source material and the crystal growth region. The high purity Argon carrier gas flows into the quartz tube from the right. (b) Photograph of several relatively large tetracene single crystals. As an indication for the size of the crystals, a standard laboratory razor blade was placed in the picture.

directions. For diffusion measurements along the c-axis of the crystals, we used both pristine and cleaved crystals. All measurements were performed on crystals that were packaged between two glass slides and sealed with an optical epoxy (Epoxy Technology) under a nitrogen environment. The absorption coefficients of the tetracene crystals were determined using a Cary 500i spectrophotometer (Varian).

We measured the spatial distribution of delayed fluorescence from tetracene and rubrene crystals. A pulsed solid-state laser beam ($\lambda = 349\text{nm}$, Spectra Physics) was delivered normal to the surface of the organic crystal. A UV-transparent microscope objective focused the incident beam to a spot diameter of $1 \mu\text{m}$ as FWHM on the crystal surface. The photoluminescence emitted by the crystal was collected by the same objective and was subsequently projected on an interline CCD camera (Q Imaging) to collect its time-dependent spatial distribution. The resolution of the resulting image was $0.63 \mu\text{m}$ per pixel. The delay between the laser pulse and the onset of data collection by the CCD camera was varied between 0 and 4 $\mu\text{s}$ using a
Figure 5-4: (a) The crystal structure of tetracene, and the definition of its crystallographic axes, with $a = 7.900 \, \text{Å}$, $b = 6.030 \, \text{Å}$, $c = 13.530 \, \text{Å}$ (b) The crystal structure of rubrene, and the definition of its crystallographic axis, with $a = 7.184 \, \text{Å}$, $b = 14.433 \, \text{Å}$, and $c = 26.897 \, \text{Å}$. Crystallographic data taken from the Cambridge Structural Database.

Pulse generator (HP). Typically, 10,000 - 40,000 frames were collected for each time-delay at an acquisition frequency of 24 Hz. We varied the laser power with the using optical density filters and monitored it with a thermal detector (Newport).

## 5.3 Experimental results

Fig. 5-5(a) shows the spatial distribution of photoluminescence emitted from the $ab$-plane of a rubrene crystal promptly after being excited by the pulsed laser. Luminescence from the excitation spot is clearly visible, as are ridge-shaped defects in the crystal surface that light up simultaneously, even though they are located tens of $\mu$m away from the excitation spot. Figure 5-5(b) compares the delayed luminescence intensity of the defect sites with that of the photoexcited spot. The decay rates at each location are the same. This observation implies that the same types of excitonic states were responsible for the delayed luminescence in both cases. This supports our previous remark that the delayed emission around the excited area on rubrene crystals are not from electronic transport, but from waveguiding.
Waveguiding of photons is a well-known physical phenomenon that occurs when light travelling within a dielectric waveguide with refractive index, $n_W$, is surrounded by a cladding medium with a lower refractive index, $n_C$. Light incident on the interface at an angle larger than the critical angle, $\theta_C$, is trapped by total internal reflection. The fraction of photons that is trapped within the waveguide, $\eta_{\text{trap}}$, is given by $\eta_{\text{trap}} = \sqrt{1 - \frac{n_C^2}{n_W^2}}$ (see Chapter 3) [59]. From this expression it follows that photons emitted from within an organic crystal ($n_W = 1.8$) surrounded by an air-cladding ($n_C = 1$), over 80% will be trapped within the crystal. The trapped photons can escape from the waveguide by scattering, as can be observed in Figure 5-5(a). The observed phenomena cannot be explained by a mere diffusion of singlets or triplets to the defect site. In such a case the defects would light up at a later moment in time than spot, which is not what we observe (See Figure 5-5(b)).
Figure 5-6: The prompt photoluminescence (column 1), the measured delayed fluorescence 1 μs after the excitation pulse (column 2), and the simulated delayed fluorescence 1 μs after the excitation pulse (column 3) for three different pump intensities creating excitons in the the ab-plane of tetracene (a-c) and rubrene (d-f). The excitation densities are (a)+(d) is $10^{20}$ cm$^{-3}$; (b)+(e) is $10^{19}$ cm$^{-3}$; and (c) and (f) is $10^{18}$ cm$^{-3}$.

Fig. 5-6 shows the fluorescence intensity distributions promptly and 1 μs after excitation by pulses of different intensities ((a)-(c) for tetracene and (d)-(f) for rubrene). The spatial profile clearly depends on the excitation pulse intensity, as the most intense pulse resulted in a spread in luminescence of $\sim 8$ μm, while the lowest pump intensity resulted in a spread of luminescence $\sim 1$ μm. Spreading of delayed fluorescence by triplet diffusion is not expected to depend on the pulse intensity, which we confirmed with simulation that we will discuss later. The observed nonlinearity is instead consistent with the waveguiding and self-absorption transport mechanism. The optical transport of triplet excitons occurs when two triplet excitons fuse to generate a singlet, which travels and becomes self-absorbed in a crystal waveguide. The rate of triplet-triplet fusion should increase as the square of their initial density [89]. We support our measurements by an optical model that simulates the triplet and singlet
densities as a function of pump intensity. This model takes into the account the effect of waveguiding and self-absorption, and will be discussed in more detail below. The results of these simulations are presented in the third and sixth column of Fig. 5-6.

Figure 5-7: (a) A photograph of the edge of a tetracene crystal. The c-axis direction and the location of the excitation spot is indicated. (b) The photoluminescence patterns after exciting the edge of the tetracene crystal shown in (a) with a laser pulse for the increasing delay times as indicated in the frames. The location of the edge of the crystal is illustrated with dotted white lines. (c) Photograph of the edge of a rubrene crystal. The direction of the c-axis is indicated by the white arrow. (d) The photoluminescence patterns after exciting the edge of the rubrene crystal of (a) with a laser pulse. Results are obtained in an identical way as figure (b). Notice the isotropic spreading of the PL over several micrometers in the different crystallographic directions.

Fig. 5-7(a) and (c) show photographs of the c-axis of tetracene and rubrene crystals, respectively, with the typical excitation spot location also indicated in Fig. 5-7(a). Figure 5-7(b) and (d) present the time evolution of the delayed fluorescence after exciting a tetracene and a rubrene crystal, respectively, along its c-axis. As can be seen, the expansion of the delayed fluorescence with time is isotropic. Identical results are obtained for the ac-plane and the bc-plane of crystalline tetracene and rubrene. This observation suggests that waveguiding is a dominant transport mechanism for triplets at high initial singlet densities (above $10^{18}$ cm$^{-3}$). Namely, triplet diffusion constants in crystalline tetracene and rubrene are calculated to be highly anisotropic; the overlap of the wavefunctions along the c-axis is minimal compared
Table 5.1: Calculated diffusion constants for tetracene and rubrene crystals in the different crystallographic directions. Experimental numbers are given in parenthesis when available.

<table>
<thead>
<tr>
<th>Crystallographic axis</th>
<th>Tetracene diffusion constant [cm² s⁻¹]</th>
<th>Rubrene diffusion constant [cm² s⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>8.05 x 10⁻³ (4 x 10⁻³ [85])</td>
<td>7.35 x 10⁻³</td>
</tr>
<tr>
<td>b</td>
<td>4.89 x 10⁻³</td>
<td>7.83 x 10⁻⁶</td>
</tr>
<tr>
<td>c</td>
<td>9.61 x 10⁻⁸</td>
<td>0.00</td>
</tr>
<tr>
<td>Total</td>
<td>1.29 x 10⁻²</td>
<td>7.36 x 10⁻³ (2.5 x 10⁻¹ [83])</td>
</tr>
</tbody>
</table>

The ab-plane and the hopping rate must be much lower in the c direction. Consequently, triplets are predicted to be much more mobile in the ab-plane than along the c-axis of crystalline tetracene and rubrene, see Table 5.1. We see that for tetracene the calculated diffusion constants are in quantitative agreement with experiments [85] and are even slightly larger. While for rubrene our calculated diffusion constant is significantly lower than that inferred from experiments [82, 83]. Furthermore, the calculated diffusion constants were found to be independent of the excitation density. The triplet diffusion are modeled using the semi-classical Marcus rate theory to get the rates and a kinetic Monte Carlo code, the details of which can be found in the paper that will be submitted based on this work.

Fig. 5-8(a) and (b) show photoluminescence patterns of the ab-plane of tetracene and rubrene at increasing delay after laser pulse illumination (t=0). All the image intensities were normalized to maximum number of photons detected their corresponding time-frame. Tetracene crystals show luminescence patterns expanding over a several micrometers in distance on a microsecond time-scale. Rubrene crystals also show increasing luminescence patterns, however, in contrast to tetracene crystals, the spot does not grow further after the initial expansion to 1 µs. Fig. 5-8(c) and (d) depict the cross-section of the photoluminescence patterns presented in Fig. 5-8(a) and (b) (see dotted lines in Fig. 5-8(a) for the area of integration), and the results of simulations of the time-resolved luminescence patterns. These simulations will be
Figure 5-8: (a) and (b) present the photoluminescence collected from the ab-plane of tetracene and rubrene crystals, respectively, integrated between the indicated delay times. The left panels of (c) and (d) show the cross-sections of the photoluminescence patterns presented in (a) and (b), respectively. The dotted line in (a) indicates the area over which the luminescence is integrated. The right panel of (c) and (d) show the result of simulations of the cross-section of the time-resolved fluorescence of tetracene crystal and rubrene crystals, respectively.

discussed in detail below.

5.4 Simulations

The four experiments described above point to waveguiding and re-absorption as a dominant mechanism of triplet transport that should be taken into account when studying triplet transport in tetracene and rubrene crystals. A quantitative description of our experimental result is desired to support our intuitive explanations of the observed effects, and to quantify the contributions of waveguiding and diffusion to triplet exciton transport. The latter is important to allow for an effective design and evaluation of organic solar cells.

We simulate the intensity-dependent and time-resolved dynamics of triplet transport by solving the rate equation for singlet and triplet populations. We consider singlet fission into two triplets and reabsorption of singlet emission. Note that we excluded triplet exciton diffusion by Dexter transfer in this simulation to evaluate
only the optical waveguiding effect on triplet transport. The distributions of singlets \( N_S \) and triplets \( N_T \) are determined by:

\[
\frac{dN_S(x,y)}{dt} = -(k_{rad} + k_{fiss})N_S(x,y) + \frac{1}{2}k_{TS}N_T^2 + k_{rad}N_S(x,y) * f_{SA}(x,y), \tag{5.1}
\]

\[
\frac{dN_T(x,y)}{dt} = -k_{trip}N_T(x,y) - (k_{TS} + k_{TT})N_T^2(x,y) + 2k_{fiss}N_S(x,y), \tag{5.2}
\]

where \( k_{rad} \) is the radiative decay rate, \( k_{fiss} \) is the fission rate, \( k_{trip} \) is the triplet decay rate for an isolated triplet, and \( k_{TT} \) and \( k_{TS} \) are the triplet-triplet annihilation rates to form high-energy triplet or singlet states, respectively [90]. We used the parameters Burdett et al. [90] for fitting the fluorescence decay in tetracene thin film; \( k_{rad} = 1.2 \times 10^8 \) s\(^{-1}\), \( k_{fiss} = 9.3 \times 10^9 \) s\(^{-1}\), \( k_{TS} = 5.0 \times 10^{-10} \) cm\(^3\)s\(^{-1}\), and \( k_{TT} = 5.0 \times 10^{-10} \) cm\(^3\)s\(^{-1}\). We obtained \( k_{trip} = 0.25 \times 10^6 \) s\(^{-1}\) by measuring the decay rate in the tails of delayed fluorescence in tetracene and rubrene crystals. \( f_{SA}(x,y) \) is the probability of reabsorption of a photon emitted at a point of \((0,0)\). \( f_{SA}(x,y) \) was calculated by performing Monte Carlo simulation on slabs of tetracene and rubrene [76]. In order to take into account the optical scattering effect that occurs while singlet emission generated in the bulk reaches the crystal surface, we calculate the final photoluminescence pattern by:

\[
L(x,y) = N_S(x,y) * f_{SC}(x,y), \tag{5.3}
\]

where \( f_{SC}(x,y) \) is the pattern of scattered light at the crystal surface for singlets created at a point of \((0,0)\).

### 5.5 Discussion and Conclusion

Our time-resolved photoluminescence imaging technique is the first study that enables to directly probe different mechanisms responsible for the transport of triplets...
in crystalline tetracene and rubrene. Both our experimental results and quantitative model support a physical picture of triplet transport in these materials in which optical waveguiding and self-absorption can play an important role besides the more conventional triplet diffusion process, and hence should not to be neglected in triplet diffusion studies. Especially at high excitation densities, which are typical for many indirect methods to probe the diffusion constants in organic materials, optical waveguiding is dominating over diffusion and is able to transport energy over several microns. Our measurements and simulations suggest that actual triplet diffusion plays a minor role in the transport of triplets at high excitation densities, and that the actual diffusion length in our measurements is below our detection limit of 0.63 μm.
Chapter 6

Conclusions and Outlook

In this thesis we focussed on improving the performance of Luminescent Solar Concentrators (LSCs). Whereas large concentration factors (> 1000) have been predicted for LSCs based on theoretical arguments, the measured flux concentration factors have been limited to values below 10 because of several loss mechanisms, two of which we directly addressed in this thesis by engineering the optical properties of LSCs at the molecular scale.

Chapter 2 concentrated on transport losses that arise from parasitic re-absorption events within the LSC waveguide. The unique optical and structural properties of phycobilisomes (PBS), a biological light harvesting complex successfully reduced the overlap between the absorption and emission spectra in the LSC waveguide. The unique self-assembled nanostructure of phycobilisomes couples a large number of donor chromophores through an internal Förster energy pathway to a handful of acceptors chromophores, reducing re-absorption losses in LSCs by approximately 50%. Since the chromophores are arranged by self-assembly, they can be cast at a low concentration into a plastic waveguide while preserving the benefits of non-radiative energy transfer, which increases the Stokes shift. By contrast, conventional LSCs typically consist of a dense film of organic dye molecules (1 µm thick) in order to achieve
effective resonant energy transfer because the synthetic chromophores are uncoupled and statistically arranged. Such conventional LSCs require the use of expensive high-refractive index glass substrates in order to prevent the light from being trapped in the thin but extremely self-absorptive organic layer. Casting should be a more cost-effective approach; therefore it is significant that we also developed a method to cast the biological complex in a solid state matrix while preserving the internal energy transfer pathway and hence its unique optical properties. While the performance of the presented PBS based LSCs is low, there are obvious paths for innovation. For instance, efficient synthetic dyes whose emission is in the near-infrared, can be coupled within the Förster radius of the acceptor chromophores. Also, the ratio between the donor and acceptor chromophores can be further enhanced by optimizing the growth conditions. While the stability and the cost of phycobilisomes might prevent their widespread implementation as dyes in LSCs, at minimum, they function as a model dye system to guide the design of synthetic dye aggregates for cast LSCs that have improved performance at high concentration factors.

Chapter 3 addressed a second fundamental loss mechanism in LSCs: trapping losses. Our approach focussed on the source of the problem: the dye emission pattern itself. We manipulated the dye emission pattern at the molecular scale so that a larger fraction of the light would be emitted below the critical angle of the waveguide. Dichroic dye molecules (which behave like dipoles) were aligned vertically with respect to the waveguide using a liquid crystal host matrix. The analytical expression we derived for the trapping efficiency of LSCs employing aligned, ideal dichroic dyes which predict trapping efficiencies above 90% for vertically aligned dipoles. The measured trapping efficiency for the vertically aligned LSC was 81%, compared with 66% for a conventional, isotropic LSC. To the best of our knowledge, the vertically aligned LSC exhibited the best trapping efficiency for any LSC reported. The improvement in trapping efficiency carried over to the overall performance; the external quantum
efficiency was 16% higher for the vertically aligned LSC than for the isotropic LSC for geometric gains up to 30. A possible downside of our approach is that the ability of vertically aligned dyes to absorb normally incident light is reduced, although the absorption at glancing angles is enhanced. We showed that adding an optical diffusers can alleviate the effect.

LSCs based on vertically aligned dyes have attractive properties for energy harvesting in windows. They preferentially absorb light that comes in at glancing angles, which is usually the situation for direct sunlight incident on a window plane. On the other hand, people actually look through a window at normal angles, where vertically aligned dyes are less absorptive.

We expect that the trapping efficiency can be further enhanced by employing dye molecules with higher dichroic ratios and by a further optimizing the liquid crystal host matrix. Also, it is important to focus on the surface roughness of the glass and coating to control the scattering losses that can also negatively impact the trapping efficiency. To enhance the absorptive capacity of an LSC that employs a vertically aligned dye for improved waveguide coupling, one would introduce isotropic or horizontally aligned dye molecules whose function it is to absorb light then transfer its energy non-radiatively to the vertically aligned dyes.

In Chapter 4, we presented a new strategy for energy harvesting in display applications. Dichroic dye molecules were aligned linearly in the plane of the LSC waveguide using a liquid crystal host, creating a high anisotropy in the absorption of parallel or perpendicularly polarized light. Linearly Polarized LSCs (LP-LSCs) could replace the purely absorptive polarizers that are conventionally used in displays to increase the contrast ratio. In a LP-LSC, the absorbed photons would be re-emitted and waveguided to PV elements in the frame of the display instead of being dissipated as heat. Our proof-of-principle LP-LSCs employing one dichroic dye molecule were able to couple 40% of the incoming photons to the edges of the LSC, while exhibiting a
polarization selection ratio of 3. The natural next step towards a successful commercial implementation of this concept is to extend the absorption of the LP-LSC over the full visible spectrum while pushing the dye emission into the infra-red.

Lastly, we focussed on the optical waveguiding process that transports photons towards PV elements. In Chapter 5, we investigated the contribution of optical waveguiding to the transport of triplet excitons in crystalline tetracene and rubrene. Our new technique allowed us to directly image the triplet distribution along the \( a, b, \) and \( c \) crystallographic axes of rubrene and tetracene crystals with sub-micrometer resolution. Our time-resolved photoluminescence imaging technique is the first to enable a direct probe of the different mechanisms responsible for the transport of triplets in crystalline tetracene and rubrene. Our experimental results and quantitative model both support a physical picture of triplet transport in these materials in which optical waveguiding and self-absorption can play an important role. This transport mechanism is distinct from the conventionally presumed triplet diffusion process, hence self-absorption and waveguiding should not be overlooked in studies of triplet diffusion. Optical waveguiding dominates over diffusion and is able to transport energy over several microns at the high excitation densities that are commonly used to probe the diffusion constants in organic materials.

To conclude, this thesis addressed two fundamental loss mechanisms in LSCs by engineering the optical properties of LSCs at the molecular scale. To carry the commercialization of LSC technology forward, the focus of research needs to shift to synthetic chemistry and materials science, where engineering truly occurs at the molecular scale. Firstly, LSC technology requires efficient and stable chromophores that emit in the infra-red and hence allow for a better utilization of the energy that is stored in the solar spectrum. The synthesis of robust dye aggregates that mimic the structure and luminescent properties of phycobilisomes can reduce transport losses in LSCs. Coupling vertically aligned dyes to isotropic absorbers can reduce trapping
losses, while also increasing the absorptivity of the LSC. Looking further ahead, one can envision exploiting photon up- and down-conversion processes in an LSC to better couple the solar spectrum to the bandgap of the solar cell. An advantage of the LSC concept is that it separates the tasks of collecting photons and generating electrical charge, allowing them to be optimized individually, as they usually are in biological systems like algae and bacteria. As in Nature, the advances that will allow LSCs to approach their fundamental performance limits will occur at the molecular scale.
Appendix A

Saturated And Efficient Blue Phosphorescent Organic Light Emitting Devices With Lambertian Angular Emission

A.1 Introduction

The development of a stable, efficient and saturated blue remains an important goal for phosphorescent organic light emitting devices (OLEDs). One important limitation is the broad photoluminescent (PL) spectrum characteristic of organic dyes. For example, greenish-blue or sky-blue phosphors have strong emission in the blue [91]. But optical transitions to higher vibrational modes of the electronic ground state extend their emission spectrum deep into the green. Because the eye responds strongly at green wavelengths, this broad emission spectrum yields an unsaturated color that is ill suited for most display applications. Unfortunately, increasing the energy of a sky-blue phosphor to minimize its green emission requires strong confinement of
Figure A-1: A schematic of a microcavity OLED with external holographic diffuser. In the absence of the microcavity the OLED emits a blue-green color. The microcavity is used to select blue emission. The diffuser corrects the angular dependence of emission from the microcavity.

excited states in the host and dye [92], limiting the molecular design possibilities. In contrast, the triplet state of a sky-blue phosphor is compatible with a broader range of host materials and sky-blue phosphors have achieved lifetimes exceeding 15,000 hours at an initial brightness of 200 cd/m[92, 93].

The color of a dye can be modified by inserting it within a microcavity [94, 95]. Indeed, a microcavity is formed within a conventional OLED by weak reflections from interfaces. But the effects of a weak microcavity on the electroluminescence (EL) are relatively minor [96]. In a strong microcavity, the dye is positioned between two highly reflective films. A strong microcavity significantly modifies the photonic mode density within the OLED, suppressing EL at undesirable wavelengths, and enhancing EL from the homogeneously broadened phosphor at the microcavity resonance.

Device Strategy In this work, we demonstrate an efficient and saturated blue phosphorescent OLED using a strong microcavity. The usual disadvantages of a strong microcavity, namely the introduction of an angular dependence to the OLEDs color, and a non-Lambertian angular emission profile, are overcome by scattering the emitted radiation [97]. See Figure A-1 for a schematic of such a microcavity OLED with an external holographic diffuser.
A.2 Device Structure and Fabrication

Figure A-2: (a) The structure of the strong microcavity OLED compared to that of a conventional, or weak microcavity OLED. In the strong microcavity the anode is a thin, semitransparent layer of Ag. The Al/LiF cathode is defined by a 1-mm-diameter shadow mask. (b) The calculated distribution of energy dissipation within the OLEDs. In the strong microcavity OLED, energy lost to the cathode, anode and waveguide modes is labeled, Aluminum, Silver and Glass, respectively. The remaining energy is outcoupled to air. The modeled layers are Ag-250Å/TPD-650Å/mCP-135Å/BCP-270Å/Al-1000Å. In the conventional, or weak microcavity OLED, some energy is dissipated in the aluminum cathode, but most energy is lost to waveguided modes. Roughly 20% of the energy is coupled to waveguide modes in the organic films. These modes are absorbed by the PEDOT and ITO layers. Another 30% is waveguided within the glass substrate. The modeled layers are ITO-1600Å/PEDOT-PSS-200Å/TPD-500Å/mCP-200Å/BCP-400Å/Al-1000Å.

The strong and weak microcavity OLED structures are compared in Fig. A-2(a). The sky-blue phosphor used in this study is FIrpic [91, 98]. The strong microcavity is formed by an aluminum cathode and a semitransparent silver anode. The weak microcavity OLED employs the conventional anode of indium tin oxide (ITO) and poly(3,4-ethylenedioxythiophene): poly(4-styrenesulphonate) (PEDOT-PSS, DuPont) rather than silver. The Al/LiF cathode is defined by a 1-mm-diameter shadow mask.

The electron transport layer is 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (bathocuprione
or BCP). To aid hole injection from the silver anode, the first 60 Å of the hole transport layer N,N-diphenyl-N,N-bis(3-methylphenyl)-[1,1-biphenyl]-4,4-diamine (TPD) is doped with 3% by mass of the acceptor tetrafluorotetracyanoquinodimethane (F4-TCNQ) [99]. The emissive layer consists of 6% by mass iridium(III)bis[(4,6-difluorophenyl)pyridinato-N,C2]picolinate (FIrpic, Luminescence Technology Corp.) in N,N-dicarbazolyl-3,5-benzene (mCP, Luminescence Technology Corp.). Devices were grown directly on the smooth back surface of frosted glass and opal glass diffusers. The holographic diffuser was employed external to devices grown on regular glass. All other layers were deposited by thermal evaporation at a base pressure of less than 3×10⁻⁶ Torr. Each layer is subject to 20% uncertainty in the interferometric measure of thickness.

A.3 Optical cavity design

The strong microcavity was designed using analytical calculations of the Poynting vector [100]. This technique allows the exact determination of the spectral dependence of energy dissipation in each layer within an OLED; see Fig. A-2(b) [100]. To optimize the color of the strong microcavity OLED, the resonant wavelength is blue-shifted by approximately 20 nm relative to the peak of the intrinsic PL spectrum of FIrpic at λ = 470 nm. At the microcavity resonance, the outcoupling fraction is calculated to be nearly 40%. The energy dissipation within the weak microcavity is also shown for comparison. Its outcoupling fraction to air is calculated to be ~30% and only weakly dependent on wavelength [100]. At the resonance, the strong microcavity enhances the photonic mode density for photons emitted in the forward hemisphere at the expense of the waveguide modes that dominate in a weak microcavity OLED [95]. The calculation also shows that most of the remaining energy in the strong microcavity is dissipated in the semitransparent silver layer, suggesting that replacing the silver with a dielectric mirror might further enhance the efficiency [95].
A.4 Experimental characterization

A.4.1 OLED Quantum Efficiency

The measured quantum efficiency of each OLED is shown in Fig. A-3(a). Collecting all photons emitted in the forward hemisphere, the peak efficiency for the strong microcavity is \((5.5\pm0.6)\)%.

The efficiency of the weak microcavity OLED is \((3.8\pm0.4)\)%,

smaller than the strong microcavity result but consistent with the expected modification in the fraction of radiation outcoupled to air.

![Graph](image)

Figure A-3: (a) The external quantum efficiency of the strong microcavity Flrpic OLED compared to the performance of a conventional weak microcavity device built on ITO/PEDOT:PSS rather than silver. The comparison demonstrates that the strong microcavity increases the efficiency of the OLED. All devices were measured in a nitrogen environment to minimize degradation. (b) The optical transmission efficiencies of our glass substrates compared to the three diffusing filters, frosted glass, opal glass and the holographic diffuser. Of the scattering filters, the holographic diffuser exhibits the highest optical transparency.

A.4.2 Transmission of Scattering filters

Although the strong microcavity enhances the efficiency, optical transmission losses in the scattering filters can be an important source of loss; see Fig. A-3(b). Three
scattering materials were investigated: frosted glass, opal glass and holographic diffusers (Edmund Optics). The holographic diffusers had a scattering angle profile of 80°. Frosted glass is formed by sandblasting the surface of glass. As shown below, it is the weakest scattering medium and it has only moderate optical transmission. Opal diffusing glass consists of an approximately 0.5 mm-thick white flashed opal film supported on glass. It strongly scatters incident light, but its optical transmission is only ~ 35%. Finally, we characterized holographic diffusers, which are formed by laser patterning of the surface of transparent polycarbonate. The holographic diffuser is ideal for this application; it is a strong scattering medium with an optical transparency of close to 100%.

### A.4.3 Angular Dependence EL Spectra

![Electroluminescent spectra](image)

Figure A-4: Electroluminescent spectra of the strong microcavity FIrpic OLED as a function of angle from the surface normal (left panel) without and (right panel) with the holographic diffuser. A solid angle cone of 0.6° was collected at each rotational position. With the holographic diffuser the color shift is barely perceptible. For comparison in (left panel) we plot the intrinsic photoluminescent spectrum of FIrpic and in (right panel) we plot the modeled electroluminescent spectrum of the strong microcavity after transmission through an ideal scattering filter.
The EL spectra as a function of angle  The EL spectra as a function of angle from the surface normal are shown in Figs. A-4, for the strong microcavity OLED without (left panel) and with (right panel) the holographic diffuser, respectively. In the left panel of Fig. A-4 we compare the EL spectra of the strong microcavity OLED to the intrinsic PL spectrum of FIrpic. The strong microcavity is observed to strongly suppress the undesirable long wavelength emission. But there is a noticeable color shift with angle. Higher wavenumbers are enhanced for large emission angles, yielding a blue shift in the EL spectrum that is constrained only by the sharp high energy shoulder of the FIrpic PL spectrum. With the holographic diffuser, however, the color shift is barely perceptible and compares well to the expected EL spectrum after transmission through an ideal scattering medium. This prediction is obtained from the intrinsic PL spectrum of FIrpic and the calculated strong microcavity outcoupling spectrum from Fig. A-2(b).

![Graph](image)

Figure A-5: The color coordinates of the strong microcavity devices with holographic diffusers are deep blue with (x,y) = (0.116±0.004,0.136±0.010). The intrinsic FIrpic photoluminescence spectrum is sky-blue with (x,y) = (0.18,0.34). Inset: the full CIE diagram identifying the expanded blue region. (b) A photograph of the resulting blue OLED. Prototype pixels are 1mm in diameter.
The color coordinates for all devices are shown in Fig. A-5(a). The average color coordinates are deep blue \((x,y) = (0.116 \pm 0.004, 0.136 \pm 0.010)\), significantly shifted from the intrinsic PL spectrum of FIrpic: \((x,y) = (0.18, 0.34)\). In Figure A-5(b) we present a photograph of the resulting blue OLED.

![Angular emission profile](image)

(a)

![Scanning electron micrographs](image)

(b)

Figure A-6: (a) The angular emission profile of the strong microcavity FIrpic OLED as a function of angle from the surface normal, together with its modification by the three diffusing filters. Opal glass and the holographic diffuser both yield nearly ideal Lambertian emission patterns. But the holographic diffuser has superior optical transparency. A solid angle cone of \(\sim 4^\circ\) was collected at each rotational position. (b) Scanning electron micrographs of the surface and cross section, respectively, of the holographic diffuser.

**The angular dependence of the intensity** In Fig. A-6(a), we plot the angular profile of EL from the strong microcavity OLEDs. In the absence of scattering, the intensity is maximized normal to the OLED stack, yielding a non-Lambertian emission profile, and potentially causing a large angle-dependent color shift if strong microcavity OLEDs are employed in display applications with conventional green and
red Lambertian OLEDs. The addition of a frosted glass filter barely alters the angular profile. The opal and holographic diffusers, however, are observed to yield near ideal Lambertian profiles, rendering these devices suitable for display applications.

Surface and cross sectional scanning electron micrographs of the holographic diffuser are shown in Figs A-6(b). The scattering film is approximately 10μm thick and lateral surface features are on the order of 5 μm. Provided the scattering film is placed within ~ 100μm of the OLEDs semitransparent electrode, a diffuser with similar or smaller feature sizes is appropriate in high definition displays.

A.5 Conclusions

To summarize, we have coupled strong microcavity OLEDs with scattering filters. The scattering filter corrects the angular dependence of EL, and the strong microcavity gives a deep blue color with enhanced optical outcoupling. The demonstrated benefits to color and efficiency suggest that this architecture - strong microcavity OLEDs combined with a scattering filter - can be generally implemented to the benefit of red, green and blue pixels in three color display applications. We also note that the maximum reported external quantum efficiency of a sky blue phosphor is nearly triple that of the control device reported here [93], suggesting that stable, saturated blue OLEDs with external quantum efficiencies exceeding 10% are within reach.
Bibliography


