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POLYMER AND DYE CHARACTERIZATION FOR OPTIMIZATION OF LUMINESCENT SOLAR CONCENTRATORS

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by

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Abstract

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With the decline of fossil fuel resources, we must turn our attention toward alternative forms of energy. Solar technology has been on the rise with decreasing costs and increasing availability, however, the large-scale application is limited by demands for an environmentally friendly approach and by land used for other necessities. Luminescent Solar Concentrators (LSCs) offer a great compromise between power production and agricultural space when implemented in greenhouses. Our design employs front facing cells that receive both direct and guided light from a fluorescent dye. This dye targets wavelengths optimal for photosynthesis and silicon solar cells. In order to increase the efficiency of the LSC panels and lower costs to make this technology widely available, we investigate alternative plastics for the LSC film and dyes that operate in the near-infrared portion of the spectrum. In this thesis we will address a new technique for film development and characterization of these materials by recording absorption and emission spectra of dyes deposited into these plastics along with relative efficiencies of the dyes.

Contents

For

my puppy Charlie,

whose love and loyalty have kept

my chin up these last few years.

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1 Introduction

1.1 How we got here

Within a few hundred years, the world will have burned through the majority of fossil fuel stores - something that took millions of years to accumulate. Predictions for continuing production over the next 50 years are bleak with production reaching a peak in the next few years, if it has not already. Fig. 1.1 shows the combined forecast of 15 models showing peak production before 2020 [1]; to meet the ever growing demand it is time to look to other forms of energy if we wish to be prepared for the years to come.
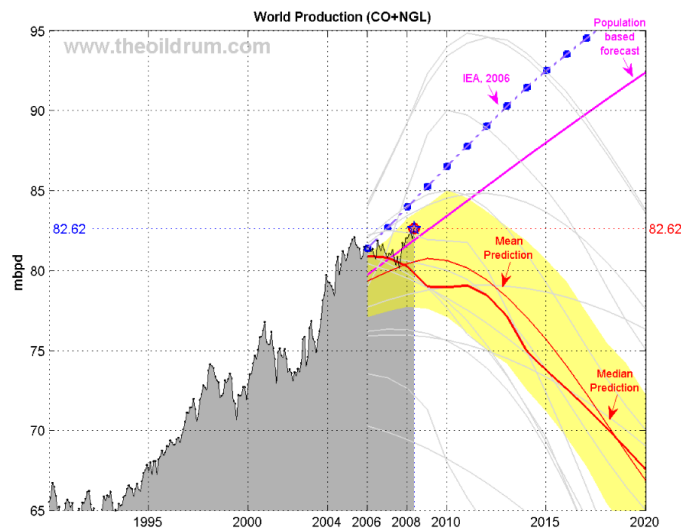

Figure 1.1: World oil production (EIA Monthly) for crude oil & natural gas liquids.

Solar energy, one of several renewable options, is an ideal choice theoretically generating 89,300 TW at the earth's surface [2] - far more than we need in a day. Even if only one percent of that power is absorbed, we should easily be able to generate enough power to make up for declining

fuel sources. And with the cost of solar heading towards $0.50/Watt, implementing it should be no problem - but where would we put all the panels?

The majority of the earth is not usable for photovoltaic (PV) technology. Between competition for agricultural production and the negative environmental impact of shading large spaces like deserts, we are left largely with spaces already in use such as parking lots and buildings. However, there is only so much usable space dedicated to those functions.

With this in mind, we look for new ways to compromise with our space-competitors. What if we could incorporate PV technology into windows, allowing light to pass through while generating power? We could certainly increase the amount of energy collected by a reasonable amount.

Enter the LSC.

1.2   What are LSCs?

Luminescent Solar Concentrators (LSCs) consist of a transparent matrix interlaced with fluorescent dyes, quantum dots, or semi-conducting polymers. Incident light is absorbed by these particles and emitted isotropically. A fraction of this light will fall within the critical angle, while the rest undergoes total internal reflection and is guided to a photovoltaic cell [3], as seen in Fig. 1.2a. This reduces the space required to generate power from the cell while allowing light to be transmitted through the medium.

The first of these systems was proposed in the early 1970s, however due to the expense and poor photostability of the system, it was not put to regular use [3]. Subsequent research and development has resulted in more efficient systems; we will focus on the improvements made using luminescent dyes.

Luminescent dyes are used in many fields such as protein marking, lasers, and protective eyewear, and they are particularly enticing for use in LSCs due to their high efficiencies and ease of dispersement in plastics. After absorbing incident light, the dye particle enters an excited state; a small amount of energy is released in the form of a phonon, resulting in the radiation of a longer
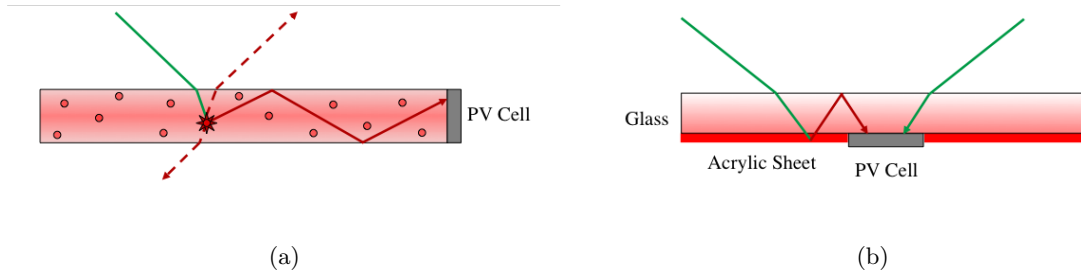
Figure 1.2: a) The standard LSC design and b) our design.

wavelength photon upon decay to the ground state. This process is known as a Stokes shift [4]. Ultimately, there is a shift in emitted light from the matrix. Ideally, this emitted light targets the active spectrum of the solar cell thereby increasing the gain (power output per cell). Dyes do not emit all light incident upon them; some is lost due to absorption. The efficiency at which they re-emit is labeled as the quantum yield of the dye [5], defined as

$$\Phi = \frac{\# \text{ of photons emitted}}{\# \text{ of photons absorbed}}.$$ (1.1)

Developments in dye technology have resulted in high quantum yield organic dyes which we have taken advantage of in our research.

Carter Labs has developed a new design utilizing a front-facing silicon photovoltaic cells which receive both direct and guided light, as seen in Fig. 1.2b, optimizing the efficiency of the solar cell. This cell is optically coupled to glass along with a 500μm polymethyl methacrylate (PMMA) sheet in which an organic luminescent dye, Lumogen Red 305 (LR305), has been deposited. The dye has a quantum yield of 85%±3% [6] and the LSC transmits 60% of incoming light. The other 40% is absorbed or redirected to the photovoltaic cell, resulting in a gain of 1.4. This dye exhibits an excitation peak at 573 nm and an emission peak at 611 nm, as seen in Fig. 1.3; we do, however, see an overlap of the absorption and emission spectra, which results in a reduction of photons directed to the cell due to reabsorption.

We have selected this dye for a very specific purpose: to eliminate competition for space by installing panels in greenhouses. By absorbing green wavelengths and emitting red, we aim to target
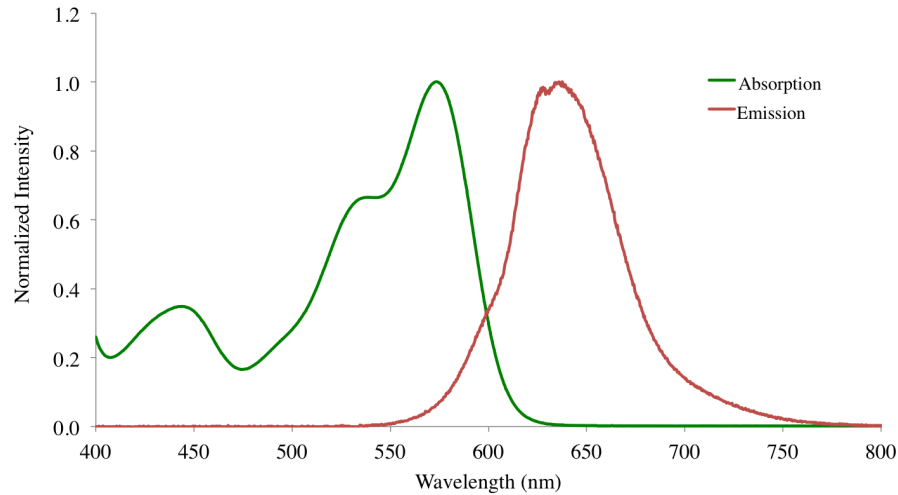
Figure 1.3: LR305 absorption and emission spectra in PMMA.

the photosynthetic spectrum of plants while increasing usable light for silicon PV cells. The LSC system is placed as greenhouse roofing, allowing necessary light to reach the plants while generating energy to operate the greenhouse. Current research indicates a neutral effect of the shifted light on the plants; however, we still need to increase the gain of the solar cells to make the installation cost-effective. To do so we continue research on polymers usable for thin films and on the addition of near-infrared (NIR) dyes.

1.3   Where we are going

To make the LSC panels ready for market distribution, we must optimize their performance in production cost, power efficiency, stability, and in the light emission for plants.

Production costs can be lowered by altering the stack - the combination of polymers, cells, and glass - we employ. This also affects the stability and lifetime of the panel. Different polymers exhibit characteristics useful in our application of LSCs. Our current design utilizes PMMA, better known as acrylic, as a medium for the dye. However, this plastic has several limitations in its cost, stability, and flexibility. This has prompted our research group to explore other polymers, especially
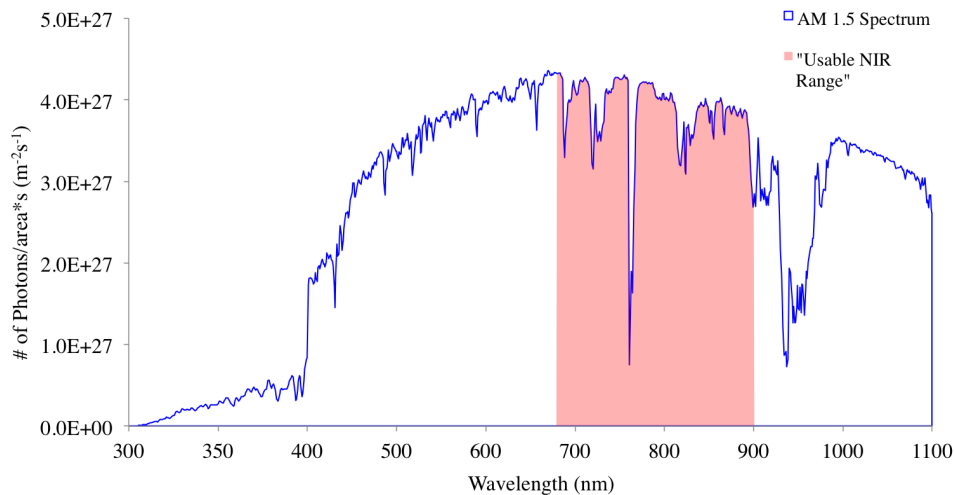
Figure 1.4: AM 1.5 Spectrum usable for silicon PV cells.

poly-vinyl butyral (PVB), that are more adaptable to our needs. The molecular structures of the polymers interact with dyes differently, resulting in varying quantum yields and excitation/emission peaks which we hope to clarify in our work.

To increase the power output of the panel without inhibiting photosynthetic processes, we begin to look towards NIR dyes. As seen in the AM 1.5 solar spectrum [7] in Fig. 1.4, the NIR region (750-900 nm) comprises roughly 35% of the usable photons for silicon, which can absorb photons up to 1100nm. That and the avoidance overlap with our dye makes this the ideal region to target. Unfortunately, dyes in this range are not known for high quantum yields, as recorded by Benson and Kues in 1983 [8]. Beginning at low concentrations they also exhibit quenching, completely failing to fluoresce. These problems are enhanced by Förster Resonance Energy Transfer (FRET) - the transfer of energy between particles without fluorescence. FRET occurs when particles are within small separation (5-10nm) and absorption/emission spectra overlap [9]. Our dye, LR305, will transfer absorbed energy to the NIR dye, resulting in a loss of energy due to the low quantum yield. This issue is easily solved, however, by separating the dyes into two matrices.

And so we set out on a quest to characterize possible polymers and NIR dyes to incorporate

into our LSC design, developing new methods and techniques along the way. In the following sections we will describe those techniques and share the preliminary results of those characterizations.

2 The Experiment

Due to their clarity and commercial availability, polyvinyl-butyral (PVB) and thermoplastic polyurethane (TPU) were selected as potential candidates to replace PMMA in the LSC stack. Butvar®B-98 was acquired for the PVB and Stevens Urethane AG8451 for the TPU sampling. PVB and TPU were tested alongside PMMA for solubility and almagamation with LR305.

The process was similarly repeated with two NIR dyes. After extensive literary research, in which there were few results, IR 125 was acquired from Exciton and ADS 775 from American Dye Source as potential NIR candidates. IR 125 had a reported quantum yield of 0.13 [8], while ADS 775 had no reported quantum yields.

2.1 Solvent testing

We began by testing the plastic and dye solubility in a variety of solvents. Plastics were tested in a 20% by weight solution on stir plates, first without heat and then heated at 80°C. Dye solubility was tested in a 5mg/mL solution, not saturated, however concentrated enough for the purpose of deposition into film.

2.2 Making the films

Typically, films are tested by spin coating onto glass or deposition by doctor blading, as is done in previous work by B. Balaban [9]. Recognizing that our new polymers have much more flexibility and would eventually be applied in a thick film, we chose to skip this step and create a new method for developing our samples, going straight to the thicker film.

After selecting the appropriate solvents for our polymer and dye combination, generally utilizing the same solvent, we dissolved 2-3 g of plastic and inserted the desired amount of dye. This
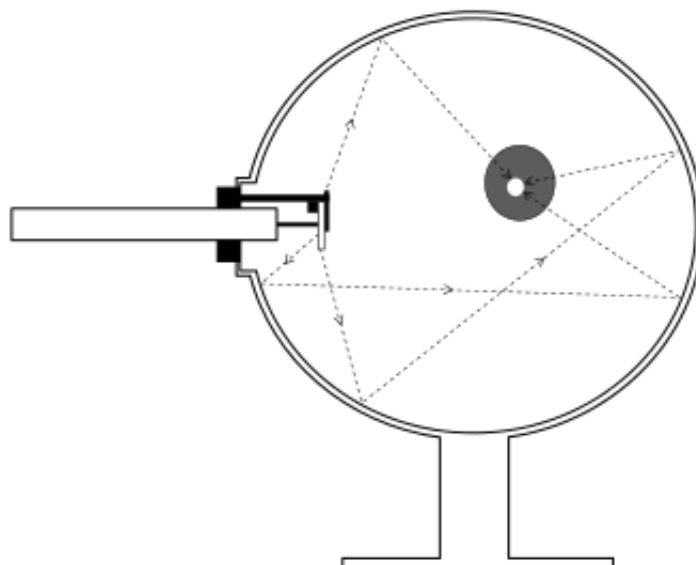
Figure 2.1: Light paths from exited dye particles in an integrating sphere.

was left to stir for 1-2 hours, allowing the dye to be evenly distributed throughout the polymer. The solution was then poured into a disposable polystyrene or aluminum dish and evaporated at low pressure and temperatures (just below the boiling point of the solvent) in a vacuum oven. Typical evaporation took 12-15 hours.

Once solidified, the dish was removed, resulting in a thick plastic puck 1-3 mm thick. It was then deposited, between two Teflon© sheets into a GeoKnight D16AP heat press. Each polymer was then pressed at its respective glass transition temperature ($\pm3°$C) for 2 minutes at 60 ± 5 psi, removed, and allowed to cool. Resulting films were 600 nm $\pm$ 75 nm. These were then cut into 10×20 mm rectangles for testing.

2.3   Characterizing the films

Films were characterized by absorption and emission spectra and relative quantum yields. Absorption spectra was taken with a Jasco V670 UV-Vis, FTIR spectrometer. Emission spectra was taken with an Ocean Optics Jaz spectrometer through an integrating sphere, shown in Fig. 2.1. A 532

nm green laser with a secondary peak at 806 nm was incident on the film, exciting molecules; light was emitted in all directions and reflected until absorbed by the spectrometer at another location. In this way, all light is captured by the spectrometer and wavelength shifts can be observed.

Relative quantum yields were calculated using the absorption and emission data produced by the spectrometers according to

$$\Phi = \Phi_{ref} \; \frac{n^2}{n_{ref}^2} \cdot \frac{I}{A} \cdot \frac{A_{ref}}{I_{ref}}, \tag{2.1}$$

where I is the integrated emission and A the total absorption of the sample and reference dye, and Φ_{ref} is the known quantum yield of a reference dye [5].

3 The Results

The three polymers were created first with no dye (for reference), then with LR305, followed by the NIR dyes. Concentration tests were also performed on the NIR dyes in PVB to determine the maximum concentration allowed before quenching occurred.

3.1 Solvents

Each polymer and dye was tested for solubility in a number of solvents, listed in Table 3.1. The dyes were not tested with all solvents, especially once it became clear the solvents did not work on the polymers. Several solvents were also abandoned after determining that the properties of the solvent were not ideal for evaporation.

Table 3.1: Solvents used and their solubility of the given material. S - Soluble, PS - Partially Soluble, SW - Swells, NS - Not Soluble. *Results proved not soluble, however previous work shows solubility.

| Solvent	PMMA	PVB	TPU	LR305	IR 125	ADS 775
Toluene	S	SW	S	S	NS	NS
Toluene:Ethanol	S	S	S	S	NS	NS
m-Xylene	S	SW	S		NS	NS
Chloroform	S	S	S	S	PS	S
Hexane	I	I	I			
Dichlorobenzene	S	PS	S			
2-Propanol	SW	S	PS	PS	NS	NS
Pyridine	S	S	S	S	PS	S
Methanol	I	S	SW	S	S	S
Octane	I	SW	I			
Chlorobenzene	S	PS	S		NS	
Dimethlysulfoxide	S	S	I	S	S	PS
Cyclohexane	I	SW	I			
4-Methylanisole	S	PS	S	S	NS*	NS
Cyclohexanone	PS	S	S	S	PS	PS
Dichloroethane	S	S	S	S	PS	S
Ethanol	S	S	SW	S	PS	PS
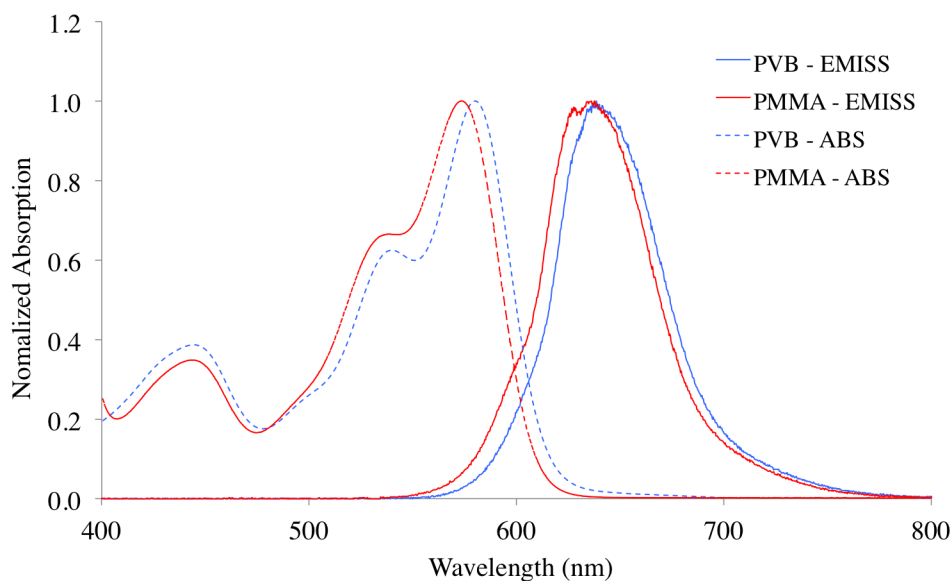
Figure 3.1: LR305 absorption and emission spectra in PMMA, PVB, and TPU.

Several solvents were found to work for almost all the materials, however in each case there was one material that was not soluble with the given solvent. Due to their ability to dissolve most of the items and their miscibility with each other, methanol and pyridine were chosen as the primary solvents used for subsequent experiments.

3.2   The films

The first films analyzed were those made with a 0.03% concentration of LR305 in PMMA, PVB, and TPU. We see a slight shift in the absorption and emission peaks, as seen in Fig. 3.1, however, only by a few nanometers. This may be due to characteristics of the dye in the polymer, solvent related issues, or error of the sampling.

We then characterized our NIR dyes in the different polymer films at 0.005% concentration. Upon creation of the films, however, we found there to be a problem with our ADS 775 samples in PMMA and TPU, in which ADS 775 in methanol was mixed with the polymer in pyridine. The films had a yellow tint as compared with the usual green coloring, indicating a wavelength shift. The

	Abs (nm)	Emiss (nm)	Stokes (nm)	Φ
IR 125				
Literature	795	833	38	0.13
PMMA	806.5	822	15.5	0.24
PVB	803	822	19	0.05
TPU	803	818	15	0.02
ADS 775				
Literature	775	818	43	-
PMMA	-	-	-	-
PVB	795	826	31	0.19
TPU	777.5	818	40.5	0.17

Table 3.2: The absorption and emission peaks, Stokes' shift, and quantum yields of IR 125 and ADS 775 in PMMA, PVB, and TPU.

polymers had not previously exhibited yellowing with pyridine in both our clear and LR305 samples, so we assumed a solvatochromatic effect on the dye - a shift of absorption and emission peaks due to the solvent used [9]. However, ADS 775 is not soluble in pyridine so the result was quite unexpected. Characterization tests were still performed, however the PMMA sample exhibited no fluorescence and the absorption spectra was significantly shifted into the lower wavelength spectrum. Results are listed in Table 3.2 along with the values provided by the manufactures, taken in solution.

Problems also arose out of the flexibility of the films. The PVB and TPU samples became bent, hindering the effects of the isotropic emission and increasing the path length of the photons, possibly increasing reabsorption effects.

Along with the peak absorption and emission wavelengths, the Stokes' shift - the change in the peaks - is recorded. Relative quantum yields are calculated, using LR305 as a reference (with $\Phi = 85\% \pm 3\%$) and the standard trapezoidal method

$$\int_a^b f(x) \; dx = (b - a) \; \frac{f(b) - f(a)}{2} \tag{3.1}$$

to calculate the integrated value between data points . Due to the poor laser quality and the variance in intensity, quantum yield values are estimated to be ±10% of the reported value.

In IR 125 we see fairly consistent peaks, also seen in Fig. 3.2a, however we see a greatly
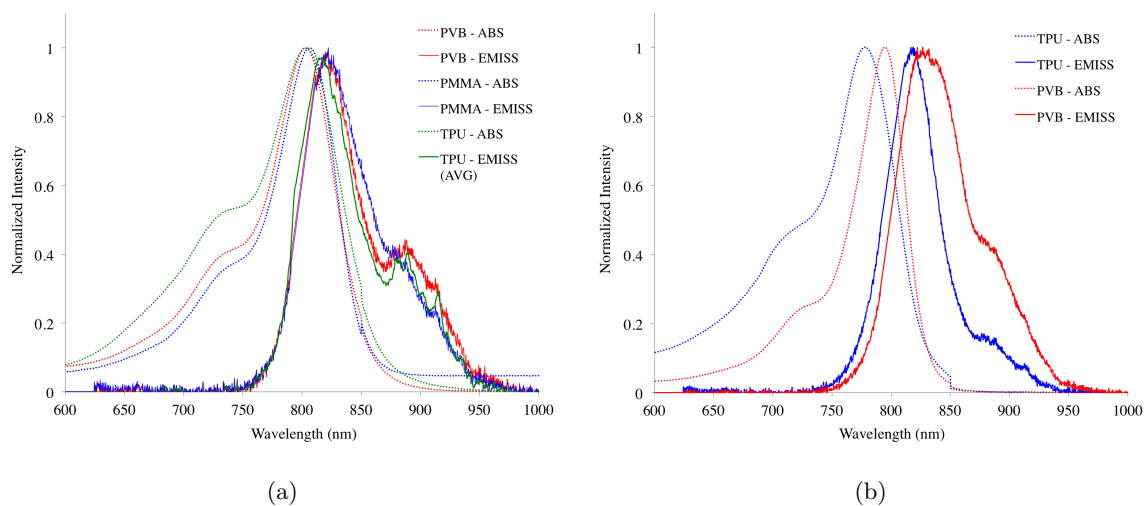
Figure 3.2: The absorption and emission spectra for a) IR 125 and b) ADS 775 in PMMA, PVB, and TPU.

reduced Stokes' shift as compared with literary values in solution. The relative quantum yield looks very positive for our PMMA film, however the PVB and TPU values appear very low. Again, this may be due to effects of the film; further testing should resolve those issues.

ADS 775 shows a bit more variation in its peaks and stokes shift, however it exhibits much greater consistency in the quantum yields. These quantum yields are quite surprising after seeing the effects the film deformation had on the IR 125 samples and the pyridine had on the PMMA sample. If, however, they are representative of the absolute quantum yields for ADS 775 in film, we can be very excited for possible applications.

In both dyes, we notice distinct shoulders in both the absorption and emissions spectra, seen in Fig. 3.2. The shoulder in the absorption spectra seems to be quite variable for the different polymers, indicating the possibility of better performance depending on the plastic choice. In IR 125 the shoulder in the emission spectra all exhibit similar intensity, which would lead us to believe similar emission ability in all polymers. In ADS 775, on the other hand, we see a significant difference in the shoulder of the emission spectra. We assume better emission properties in our PVB sample over the TPU sample.
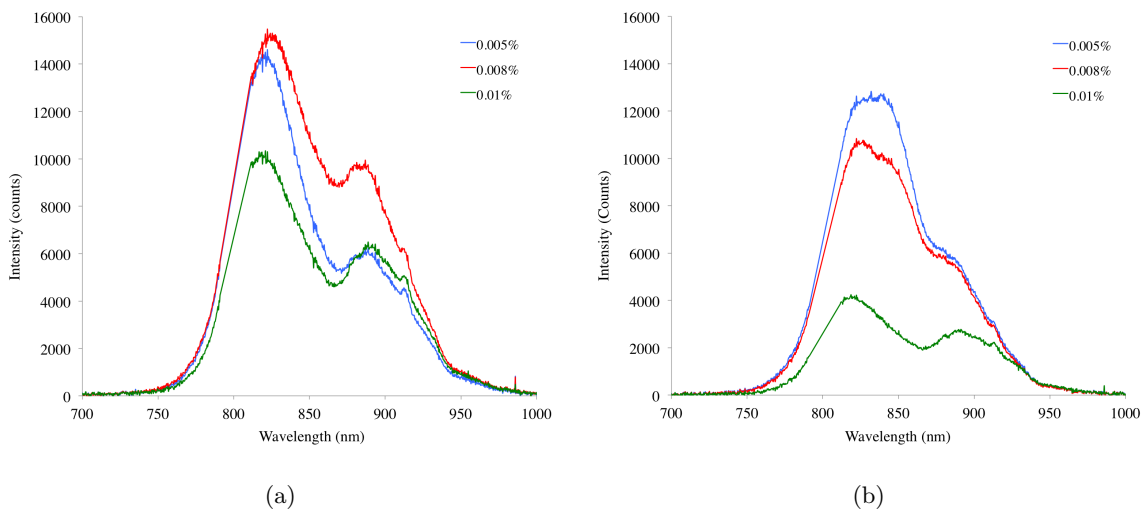
Figure 3.3: Emission spectra of a) IR 125 and b) ADS 775 samples of varying concentration in PVB.

We now turn our attention to our concentration studies. PVB samples with 0.005%, 0.008%, 0.010%, 0.030%, and 0.050% concentrations of dye underwent emission measurements. Emission spectra for the first three concentrations are shown in Fig. 3.3; spectra for the latter two concentrations are omitted, as they had completely quenched and had no viewable emission.

In our IR 125 samples, we see the increasing emission from our 0.005% to 0.008% sample but a clear decline from 0.008% to 0.010%. This indicates quenching beginning around 0.008% concentration; further tests must be done at smaller intervals to be certain of the maximum concentration possible.

The ADS 775 sample, shows quenching beginning at even lower concentrations. Quenching may begin somewhere between 0.005% and 0.008%, however fast decline in emission indicates quenching beginning even lower than 0.005%.

4   A Short Discussion - What Now?

We have looked at several ways to reduce costs and increase productivity of the LSC panels. However, there is still a great amount of work to do.

Though the polymers tested showed positive results in combination with LR305, they are still undergoing lifetime and stability tests to determine if they can meet the demands of panels set in place for a minimum of 10 years. This includes studies of the dye incorporated into the polymers and learning how the dye behaves for extended amounts of time. Work is being done to determine the optimal stack for our LSCs, including researching back sheets and other requirements to make these new polymers work in a greenhouse environment. New polymers are still being found and brought in as potential replacements, requiring more work of the same nature as the experiments discussed in this thesis.

Work on improving the efficiency of the LSCs is an on going process. The work presented on the NIR dyes is very preliminary and a more in depth characterization is needed. That we can see fluorescence from the dyes at all is quite impressive and a huge accomplishment; this gives us incentive to continue our work. The unexpected solvatochromatic effects indicate that a better understanding of the dyes is necessary and more solvent tests must be performed to control those effects in the future. Additionally, the quenching effects of the dyes are occurring at much lower than expected concentrations. Once integrated into the system, this may cause the dye to have little effect on the overall gain the PV cell experiences.

Along with more rigorous testing of the spectra and quenching effects, we must also address the quantum yields. Absolute yields must be calculated, something that would benefit the community greatly. Once these characteristics have been investigated, we must do lifetime studies similar to those being performed on LR305 now. We must do path-length analysis to find the effects of reabsorption on the dyes as well as look at the effects of FRET on the combined system of the

NIR dye with LR305.

Several other possibilities exist for our work with NIR dyes as well. Other dyes, typically used as biomarkers, are reported to have much higher quantum yields and may be able to be incorporated into the plastics. We may also begin work with metal enhanced fluorescence (MEF), which has been shown to increase the quantum yield of fluorophores [10].

In addition to the NIR, have other ranges of the spectrum to explore, including the replacement of LR305 with a dye better suited for targeting photosynthesis. Currently we are not utilizing the UV-Blue range of light, which can be shifted to blue, green, or red wavelengths, all enhancing the efficiency of the panel.

Our goals are within sight. Studies are in place at greenhouses, research is progressing, and we are making great headway on this project. With the number greenhouses covering the earth's surface, implementing our panels on just a few may make a big difference. Work on the dyes outside the visible spectrum may prove useful in creating LSCs that are completely clear - something that could be used on any building, not just in greenhouses. With this work, we have begun taking steps towards a brighter and more stable future free of dependence on fossil fuels.

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