A Characterization of Small Molecule and Polymer Dyes for Use in Luminescent Solar Concentrators

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Abstract

The use of luminescent solar concentrators (LSCs) in conjunction with solar cells is an option to make solar power more cost effective. This thesis details the physical processes that that aid and hinder the effectiveness of an LSC: fluorescence, absorption, emission, life time effects, total internal reflection, and quantum yield. Additionally, the luminescent dyes Rhodamine 101, Grand Red, Arkansas Violet, Red Polyfluorene (Red F), Red O, and RP 231 will be characterized in order to determine if their use in LSCs would be advantageous. Ultimately, it is shown that the dyes Rhodamine 101, Red Polyfluorene, RP 231, and Red O have the highest potential for implementation in LSCs.

Acknowledgements

I would like to thank my family, who facilitated and encouraged my interest in science and physics. I would like to thank all my friends who made studying for classes more manageable and enjoyable. I would like to thank Professor Sue Carter for allowing me to work in her lab, and use the equipment and supplies I needed to complete this project. Finally, I would like to thank Dr. Yvonne Rodriguez for helping me analyze my data and for proofreading this thesis.

Introduction

Over the past decade, there has been an increasing trend towards “going green” in our society. This can likely be attributed to the realization that we live on a planet with finite resources. Some of the primary resources that will soon be in short supply are the fossil fuels; coal, oil, natural gas, etc. In addition to their short supply, fossil fuels are also the major contributors of carbon dioxide and other pollutants to the atmosphere. Carbon dioxide and other greenhouse gasses are generally linked with the global warming trend, as well as ocean acidification. [1] In addition to these long term effects, where full outcomes are unpredictable, fossil fuels have many immediate consequences. The recent disaster of the Deep Horizon oil rig in the Gulf of Mexico reminds us that we can easily lose control over this toxic material. The monetary costs alone are estimated to exceed hundreds of millions of dollars. [2] Future catastrophes like this one can be avoided by lessening our reliance on fossil fuels.

A prime candidate for an alternative energy source is solar power. The potential for solar photovoltaics is enormous, with the intensity of direct sunlight on the earth’s surface exceeding 1000 W/m^2. [3] Photovoltaic technology is improving rapidly and methods of creating more efficient solar cells are being developed every year, but the industry is still being held back by cost. The price of solar generated electricity can run up to approximately \$3 per Watt. [4]

The best way to reduce the costs of solar cells is simply to use less material. By concentrating light onto a smaller area, the price of a photovoltaic system can be cut drastically. The standard ways of concentrating involve using lenses or mirrors to refract or reflect light onto a smaller area. Unfortunately, all that intense light starts to heat up the solar cell, and it has been demonstrated that the efficiency of a photovoltaic cell deteriorates as temperature increases. [5] Another difficulty for traditional concentrators is that they must track the path of the sun in order to ensure that the light is directed to the correct point. The electronics and motors required to track the sun add a significant cost to the system.

An alternate method of concentrating light is the use of luminescent solar concentrators (LSCs). An LSC is made up of a luminescent dye in a transparent substrate, usually glass or plastic, with photovoltaic cells placed around the edges. Light enters the face of the substrate, where it is absorbed by the dye. The dye reemits another photon at a longer wavelength, which is waveguided to the edge of the substrate via total internal reflection. When the new photon reaches the edge, it can be absorbed by the photovoltaic cell. For a diagram of an LSC, see figure 1. Sunlight incident to the face of a sheet of glass gets concentrated onto the area of the edges.

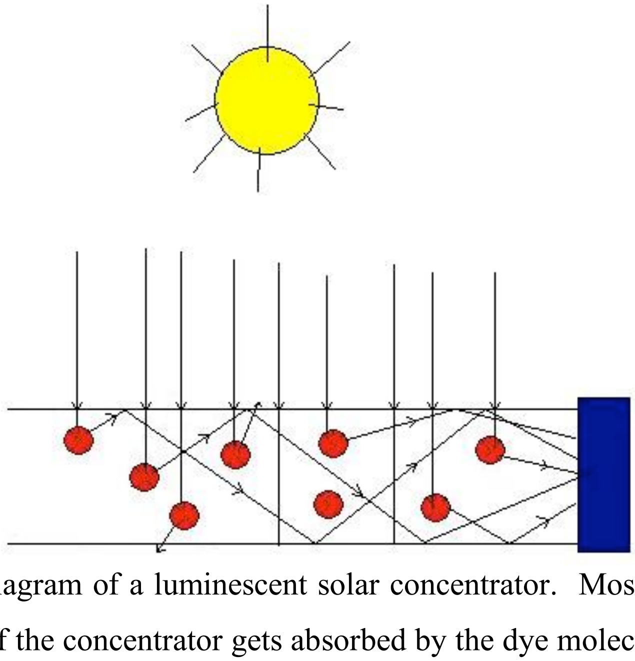

Fig. 1. A Simple diagram of a luminescent solar concentrator. Most of the sunlight that comes in the face of the concentrator gets absorbed by the dye molecules and is reemitted to a small area photovoltaic cell on the edge.

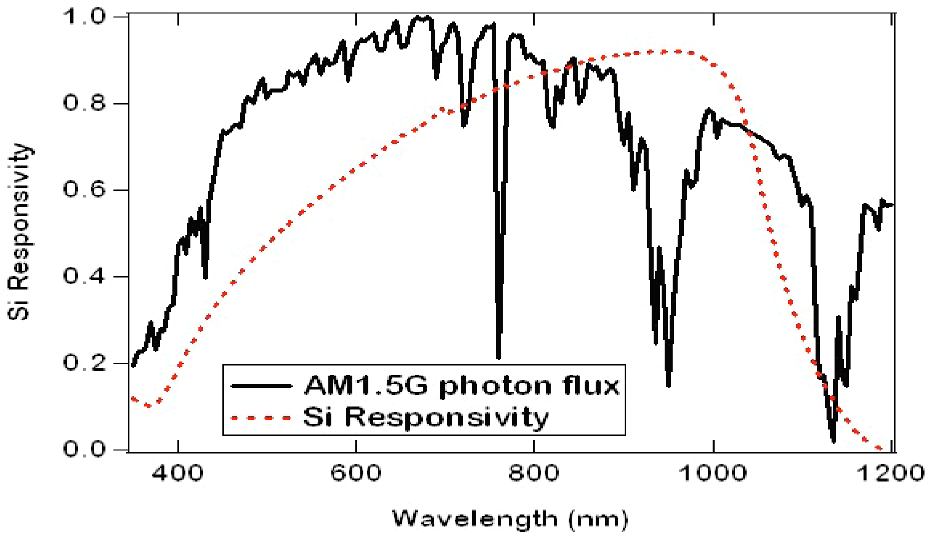

Fig. 2. The emission spectrum of the sun normalized to the responsivity of silicon. The peaks of the solar spectrum and silicon's responsivity do not match up. (Olson 2009)

Covering an area with dyes on glass or plastic is far cheaper than covering an area with solar panels. Additionally, the peak responsivity of silicon solar cells is around 1100 nm, but the majority of sunlight is in the shorter, visible wavelength spectrum. See figure 2. When a photovoltaic cell absorbs a photon with energy greater than the band gap of the cell, the excess energy is converted into heat. Luminescent dyes emit most of their light at longer wavelengths than they absorb, so the light that the solar cells absorb is closer to the peak of the responsivity. This means the solar cells absorb light more efficiently, and the LSCs do not heat up the solar cells. Also, LSCs do not need to track the sun because they work just as well, if not better, in diffuse light rather than direct light. [6] A more aesthetically beneficial aspect of LSCs is that they can be easily incorporated into windows or skylights, thus using the light that is not absorbed by the dye to illuminate rooms indoors.

This thesis will detail the key concepts of luminescent solar concentrators; such as fluorescence, emission and absorption spectra, total internal reflection, and quantum yield. Additionally, some hurdles that must be overcome will be addressed; such as light cone loss, self absorption, and photobleaching. Specifically, the small molecule dyes Rhodamine 101, Grand Red, and Arkansas Violet, and the polymer dyes Red Polyfluorene (Red F), Red O, and RP 231 will be explored. These dyes were chosen because they all absorb in the peak of the solar spectrum and emit in red wavelengths. The concentration dependence of Rhodamine will be determined, and the quantum yield of Grand Red, Arkansas Violet, Red F, Red O, and RP 231 will be calculated using several techniques. Based on the performances of the dyes, it is suggested that more research be done on Red F, RP 231, and Red O for use in luminescent solar concentrators because they have relatively high quantum yields and the least self absorption. Also, Rhodamine is also a likely candidate because its high quantum yield makes up for its self absorption.

Fluorescence

The phenomenon known as luminescence is the excitation and subsequent relaxation of an electron in an atom or molecule. The defining factor of luminescence is emission of light during the relaxation of the electron. The initial excitation can be caused by a number of processes; including chemical reactions, frictional motion, application of an electric current, absorption of light, etc. [7] When a molecule undergoes luminescence due to the absorption of a photon, the process is called photoluminescence. Photoluminescence can be further divided into two different categories: fluorescence and phosphorescence. The difference is that phosphorescence occurs on much longer time scales than fluorescence. The dyes used in LSCs generally undergo fluorescence.

At normal temperatures the electrons of a fluorescent molecule, or fluorophore, will typically be in the ground state energy, S_0. When a photon of energy $E = {}^{hc}\!/_{\lambda}$, hits an electron, the photon will be absorbed if E is greater than or equal to the energy difference between S_0 and S_1 (or S_2, S_3, etc.) The value h is the Planck's constant, c is the speed of light, and λ is the wavelength of the photon. Within each of the energy levels, there are many additional sub-states, including vibrational energy levels. When the electron is excited to a higher energy state, it is also excited to some vibrational energy level. The electron soon looses the vibrational energy as heat or other non-radiative processes. It then falls back to the ground state as it emits a new photon with energy $E` = {}^{hc}\!/_{\lambda`}$. This process is shown with a Jablonski diagram, figure 3.

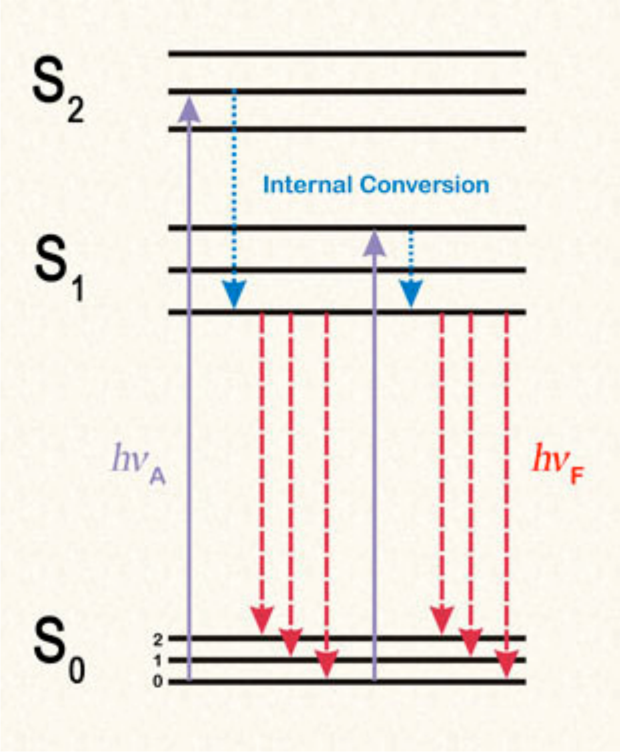

Fig. 3. [8] A Jablonski diagram showing possible energy levels of an electron. Different wavelengths of absorbed light lead to similar wavelengths of light emitted.

It is rare for an emission spectrum of a dye to exhibit a narrow peak of just a few nanometers. Since there are so many vibrational levels within each energy state, the emission spectrum can be a wide peak or band across wavelengths. The large amount of vibrational levels means that there are many radiative "paths" for the electron to take to return to the ground state. Each path has a slightly different energy and corresponds to a slightly different color of emitted photon. However, the relative intensities of the different wavelengths emitted will usually be the same, regardless of the wavelength of light absorbed. The wavelength of the light emitted will not necessarily change when the wavelength of the incident light changes. The absolute intensity of emitted light will vary with the wavelength of the incident light, though, because different wavelengths may be more or less likely to be absorbed by the fluorophores.

Not all of the paths, however, will result in the emission of a photon. The electron can return to the ground state by losing energy through heat, rather than a photon. Additionally, as the time goes on, the fluorophore will be less likely to emit. This can be caused by several mechanisms. While the fluorophore is in its excited state, there is a higher possibility for it to undergo a chemical reaction. When the chemical structure of the molecule is altered, the energy states change as well, eliminating the radiative path. This process is known as photobleaching. Another way for the dye to fade is exposure to molecular oxygen. Since oxygen is a highly reactive molecule, oxygen will cause the fluorophore to oxidize. [9] Similar to photobleaching, when the dye is oxidized, its chemical structure is altered, thus preventing emission of a photon.

Emission and absorption spectra

There are several ways of describing the optical properties of a material, but they all can be derived from Beer's Law, which states that the intensity of the light is $I = I_0 e^{-\varepsilon Mx}$, where I_0 in the incident intensity, ε is the molar absorptivity, M is the molar concentration, and x is the pathlength of the light. The transmittance, which represents the fraction of light that passes through length x, goes as $T = \frac{I}{I_0} = e^{-\varepsilon Mx}$. The absorbance, also known as the optical density, is

$$D = -\ln T = \varepsilon Mx\,. \qquad \text{Eq. 1}$$

It is a unitless quantity and it represents the linear dependence on concentration of absorption. The absorbtance, not to be confused with the absorbance, goes as

$$A = 1 - \frac{I}{I_0} = 1 - T\,, \qquad \text{Eq. 2}$$

if losses of intensity due to reflections are ignored. The absorbtance represents the fraction of light that is absorbed relative to the incident light.

When the peaks of the emission and absorption curves overlap, a problem arises. Shorter wavelength light emitted has a chance of being reabsorbed by other fluorophores, in a process known as self absorption. Self absorption is problematic because most dyes do not always emit a photon after absorbing one. Self absorption is often quantified by taking the difference in wavelengths of the emission and absorption peaks. This is called the Stokes shift. Generally, a large Stokes shift is desirable for LSCs because it means most of the photons being emitted are at a wavelength much longer than the wavelength which is absorbed the most. Unfortunately, the Stokes shift is not enough information, because some dyes may have long tails that extend away from the peak, and other dyes will have steep drops close to the peak.

Total internal reflection

When the light is emitted from the fluorophores, it will be emitted in a random direction. A photon will go on its way until either it gets reabsorbed by a different molecule, or it comes to a boundary between two mediums. The index of refraction of the substrate is often similar to the index of refraction of the solvent or dye, so that boundary affects the path of the photon very little. However, the boundary between the air and the substrate is critical to the success of the LSC.

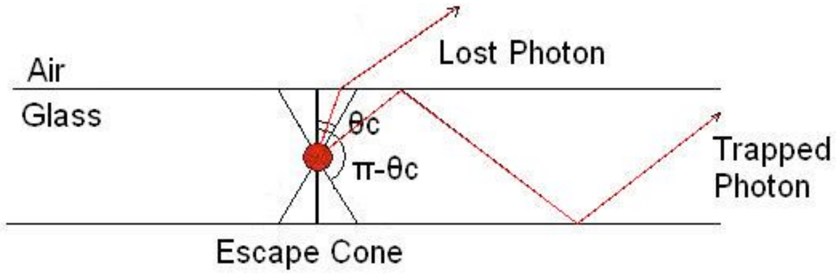

Fig. 4. Possible paths for an emitted photon. Photons emitted at angles less than the critical angle on either boundary will be lost.

When a photon originates in some medium with a larger index of refraction than an adjacent medium, the light will either pass through to the new medium or be reflected back in the original medium. Whether or not it reflects depends of the angle of incidence of the photon with respect to the normal of the boundary. If the angle is greater than some critical angle, θ_c, then all the light will be reflected, as in figure 4. The critical angle can be solved for using Snell's Law, $n_1 \sin\theta_1 = n_2 \sin\theta_2$, where n_1 is the index of refraction of the original medium, n_2 is the index of refraction of the second medium and is smaller than n_1, and θ_1 and θ_2 are the angles of the light paths relative to the normal of the boundary for the mediums. [10] If $\theta_1=\theta_c$, then $\theta_2=\pi/2$, and Snell's law can be rewritten as $\sin\theta_c = \frac{n_2}{n_1}$. If $n_2=1$, as it is for air, then

$$\sin\theta_c = \tfrac{1}{n}. \qquad \text{Eq. 3}$$

Unfortunately for LSCs, not all of the photons will be emitted at an angle that will undergo total internal reflection. Some of it will be lost through the so called "light escape cone." To understand what affect this has on the overall efficiency of the concentrators, it is necessary to calculate the fraction of light trapped. The total light emitted is assumed to be evenly distributed over the solid angle of a sphere:

$$\int_0^{2\pi}\int_0^{\pi}\sin\theta d\theta d\phi = 4\pi. \qquad \text{Eq. 4}$$

Assuming the boundaries are parallel planes, the solid angle of light trapped by total internal reflection is

$$\int_0^{2\pi}\int_{\theta_c}^{\pi-\theta_c}\sin\theta d\theta d\phi = 4\pi\cos\theta_c. \qquad \text{Eq. 5}$$

Recalling equation 3 and several trigonometric identities, the previous equation can be rewritten

$$4\pi\cos\theta_c = 4\pi\tfrac{\sqrt{n^2-1}}{n} = 4\pi\sqrt{1-\tfrac{1}{n^2}}. \qquad \text{Eq. 6}$$

The fraction of light trapped, L, with respect to all of the light emitted is the ratio of equations 6 and 4, and it goes as

$$L = \sqrt{1-\tfrac{1}{n^2}}. \qquad \text{Eq. 7}$$

For material with indices of refraction of around 1.5, such as glass, L=0.75. This means about 75% of the light emitted will be trapped by total internal reflection, and 25% will be lost to the air.

Quantum Yield

The quantum yield, φ, of a fluorophore is defined as the ratio of the number of photons emitted by the molecule and the number of photon absorbed. [9] It is important because it represents the maximum fraction of light that can be harvested by the photovoltaic cells. The first method of measuring the quantum yield that comes to mind involves counting all the photons absorbed and emitted. This would be a tedious task and would require the use of an integrating sphere. An alternate method makes use of fluorescence and absorption spectrometers. The number of photons emitted is proportional to the intensity of the emission spectrum, I_{em}, integrated over all wavelengths, λ. However, because the light is observed out of the medium it originated from, the square of the index of refraction, n, of the solvent is multiplied by the intensity. The number of photons absorbed is proportional to the intensity of the excitation spectrum, I_{ex}, multiplied by absorbtance, A, integrated over all wavelengths. The quantum yield for some sample dye can now be written as:

$$\varphi = \frac{n^2 \int I_{em} d\lambda}{\int I_{ex} A d\lambda}. \qquad \text{Eq. 8}$$

Unfortunately, there is some unknown geometric factor due to the fact that not all of the light emitted is measured by the spectrometers. This can be accounted for by comparing the sample to some standard with a known quantum yield. The equation for quantum yield becomes:

$$\varphi = \frac{n^2 \int I_{em} d\lambda \int I_{exS} A_S d\lambda}{n_S^2 \int I_{ex} A d\lambda \int I_{emS} d\lambda} \varphi_S, \qquad \text{Eq. 9}$$

where the subscript S represents the standard.

A third method of measuring quantum yield can be used. The emission and absorption spectra of the sample and the standard are scanned at several different concentrations. The integrated intensity of the emission spectrum is plotted against the absorbance (not absorbtance) which corresponds to the peak of the excitation curve. [11] A linear approximation is generated, and the equation

$$\varphi = \varphi_S \left(\frac{n}{n_S}\right)^2 \left(\frac{b}{b_S}\right) \qquad \text{Eq. 10}$$

is used to find the quantum yield, where b is the slope of the line. [12] It is reasonable to use a linear regression for luminescent intensity versus absorbance because both quantities have a linear relationship with concentration. When concentration increases, the number of fluorophores increases by the same factor, which leads to the number of photons emitted increasing by the same factor. As seen in the equation for absorbance (equation 1), there is a linear dependence on concentration.

When taking quantum yield measurements, care must be taken when choosing the concentration of the samples. This is because as concentration increases, so does the optical density. As the optical density increases, a larger fraction of the light is absorbed for a given path length. With more absorption, the emission spectrum will have a greater redshift. Additionally each time a photon is absorbed, it becomes less likely for it to make it to the detector due to self absorption. It is recommended that optical density is less than 0.1 for wavelengths at and longer than the excitation wavelength. [12]

Methods

The dyes Rhodamine, Grand Red, Arkansas Violet, RP 231, Red O, and Red F were examined. All of the dyes were chosen because they absorb the peak of the solar spectrum and emit in the red end of the visible spectrum. This is favorable because a majority of the sunlight should be absorbed, then reemitted as close to silicon's peak responsivity as possible. In order to measure the amount of light emitted or absorbed by these dyes, first a highly concentrated stock solution was made by dissolving in a solvent. The mass of dye, the type and volume of solvent, and the concentration of each stock solution can be seen in table 1. To ensure mixing, a magnetic stir bar was placed in each vial, and the vials were placed on a magnetic stir plate. The solutions were allowed to stir overnight before creating the sample solutions. A list of the concentrations scanned for each dye is shown in table 2. No stock solutions were made for Red O and RP 231. They were obtained pre-mixed in chlorobenzene. The concentrations of Rhodamine are given in percent by mass, as well as molarity. Molarity (M) is defined as the number of moles of a substance per liter of solvent. The molar mass could not be determined for any of the other dyes.

The Rhodamine samples were scanned in order to study the concentration dependence of dyes. It was also used as a standard of comparison when measuring the quantum yield of the other dyes because it is known to have a quantum yield of 1 under certain conditions. [13] For the third method of measuring quantum yield, the same concentrations of Rhodamine, Red F, Grand Red, and Arkansas Violet were used as the second method, however, slight alterations in the concentration were made, but they are of the same order of magnitude.

All of the properties investigated involved taking photoluminescence and transmission data. Approximately 2.5 mL of each of sample solution was placed in a quartz cuvette with an optical pathlength of 10 mm. Then the cuvettes were scanned, one at a time, by an N&K Analyzer in order to measure the transmittance, and a Perkin Elmer LS 45 Fluorescence spectrometer to measure the luminescent intensity. The luminescent intensity is measured in arbitrary units, and the transmittance is unitless. Before scanning the transmission, a baseline scan was taken for a cuvette without dye, but full of solvent. The baseline factors out transmission losses due to the solvent and cuvettes.

Stock Solution	Solvent	Mass of dye (g)	Volume of Solvent (mL)	Concentration (mol/L)	Concentration (% by mass)
Rhodamine	Ethanol	0.025	3.0	1.4x10^{-2}	1
Rhodamine	Ethanol	0.005	6.0	1.4x10^{-3}	0.1
Red F	Chlorobenzene	0.003	6.0	N/A	0.04
Grand Red	Toluene	0.002	6.0	N/A	0.04
Arkansas Violet	Toluene	0.001	6.0	N/A	0.02

Table 1. Quantitative descriptions of the each of the stock solutions created

Dye	Concentration % by mass (M)	Dye	Concentration % by mass
Rhodamine	0.03 (5x10^{-4})	Red O	0.01
“	0.003 (5x10^{-5})	RP 231	0.01
“	0.001 (2x10^{-5})	Red F	9x10^{-6}
“	6x10^{-4} (9x10^{-6})	Grand Red	1x10^{-5}
“	1x10^{-4} (2x10^{-6})	Arkansas Violet	4x10^{-4}
“	3x10^{-5} (4x10^{-7})		

Table 2. Concentrations scanned for each dye.

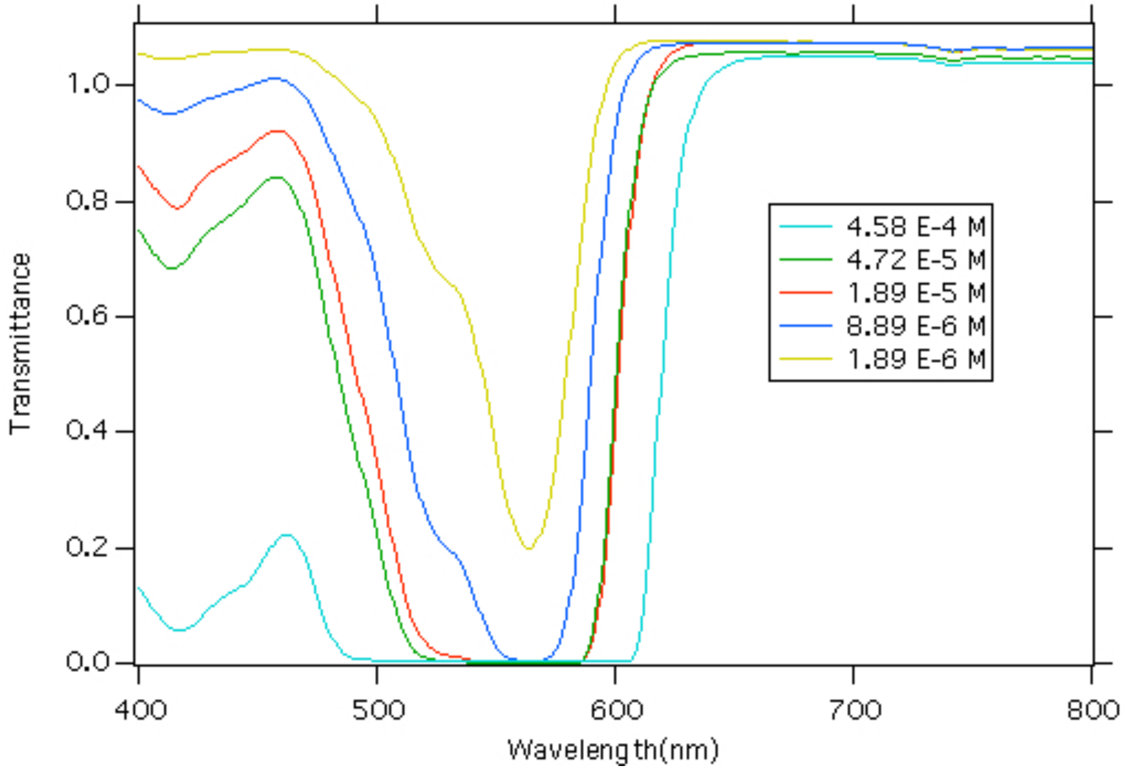

Fig. 5. The recorded transmittance data for five concentrations of Rhodamine.

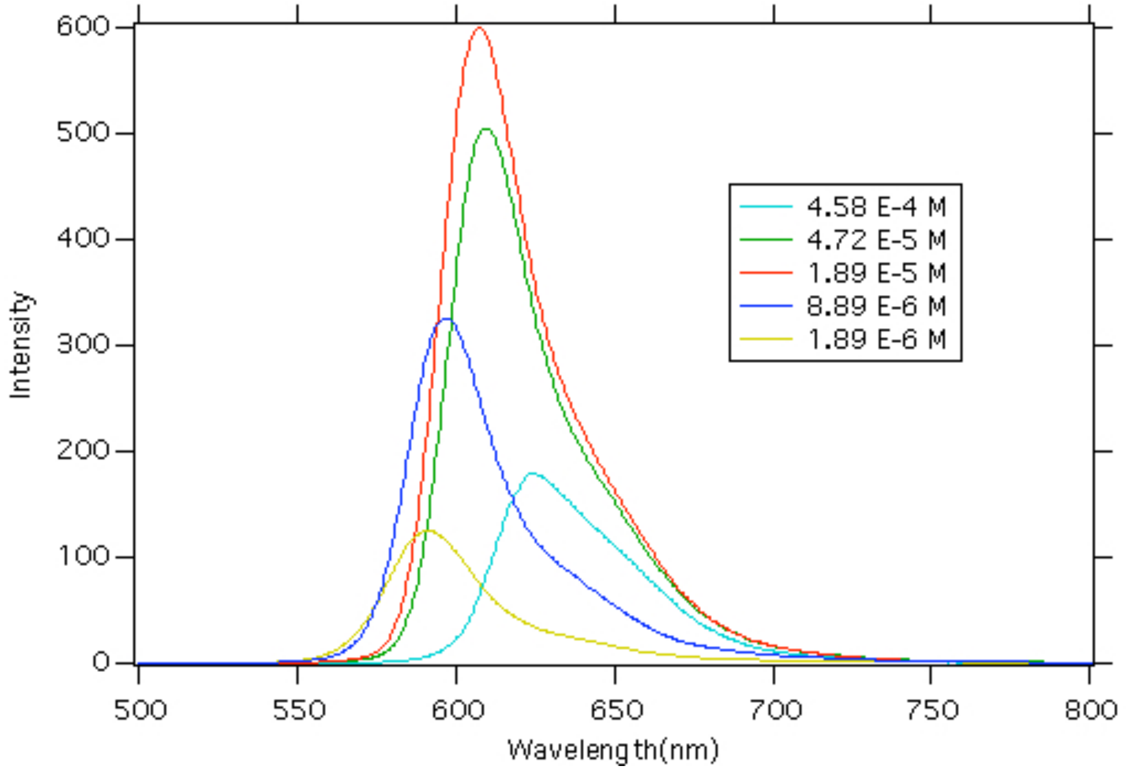

Fig. 6. The recorded luminescent intensity for five concentrations of Rhodamine.

Results and Analysis

To scan the photoluminescent intensity of Rhodamine, the different concentrations were excited with 300 nm wavelength light. The results of the transmission and emission curves for five concentrations of Rhodamine can be seen in figures 5 and 6. Using equation 2, the transmittance spectra were used to calculate the absorbtance spectra for each of the concentrations, which are displayed in figure 7. It is clear from figure 7, as the concentration increases, more light is being absorbed. This is to be expected because there are simply more molecules obstructing and absorbing the light.

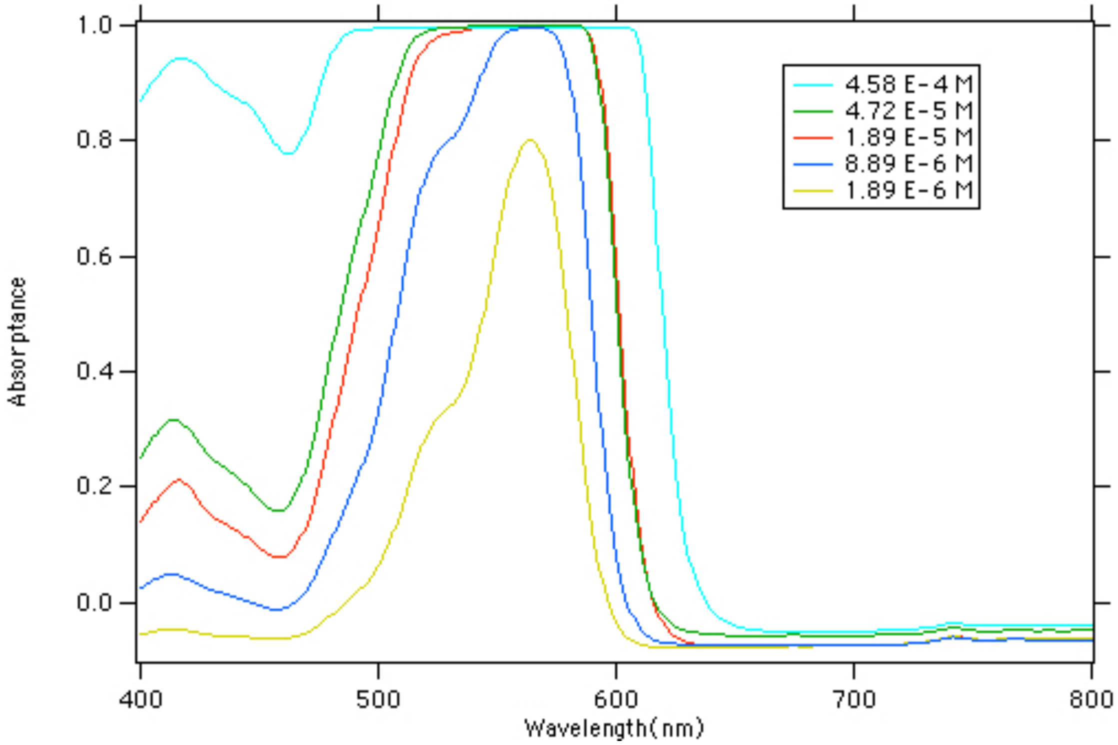

Fig. 7. The calculated absorbtance data for five concentrations of Rhodamine.

By plotting the wavelength of the emission peak of Rhodamine versus concentration, figure 8, a distinct redshift can be seen with higher concentrations. As previously noted, when the concentration increases absorbtance increases as well. Since there is a higher chance of being absorbed in a higher concentration, the photons will have a shorter average pathlength before being reabsorbed. This means there will be more excitation emission cycles before reaching the edge. Each time a photon is absorbed, if it is re-emitted, it must be at an equal or longer wavelength, hence a redshift.

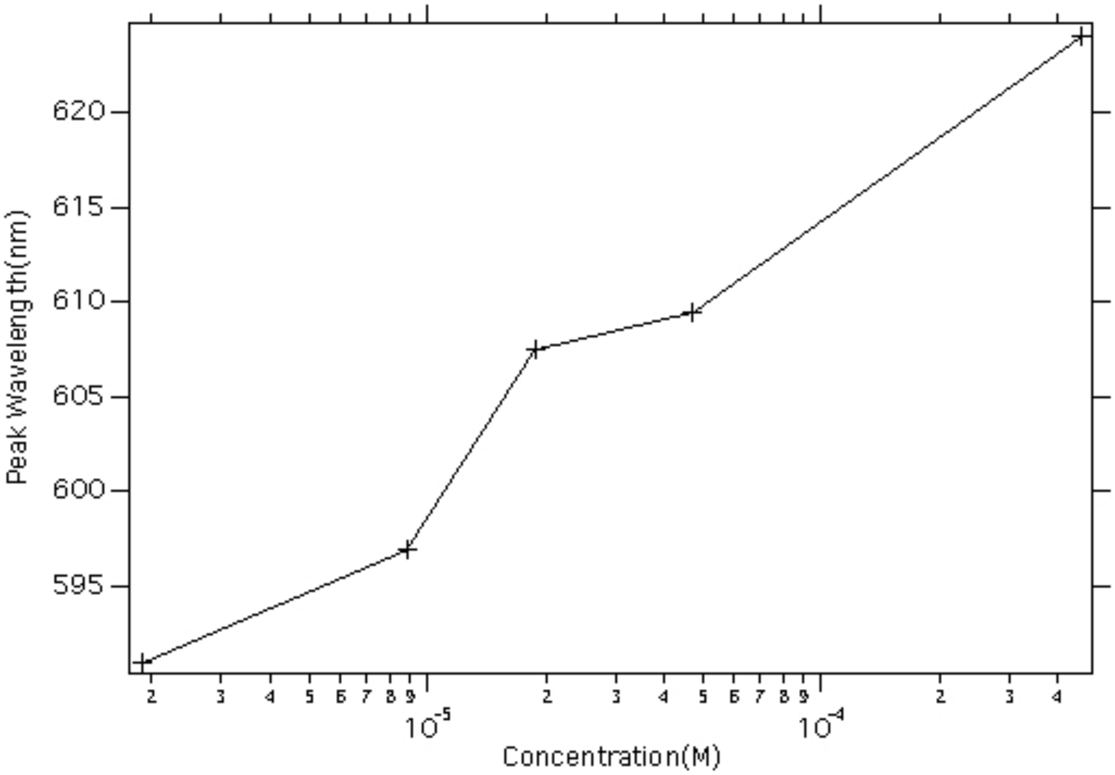

Fig. 8. The emission peak wavelength as a function of concentration for Rhodamine.

Figure 9 plots the intensity of the emission peak versus the concentration for the five samples of Rhodamine. As concentration varies, there are two competing factors involved with respect to overall emission intensity; as concentration increases, there are more fluorophores emitting, which increases the intensity, but the fluorophores also absorb the light, which reduces the intensity.

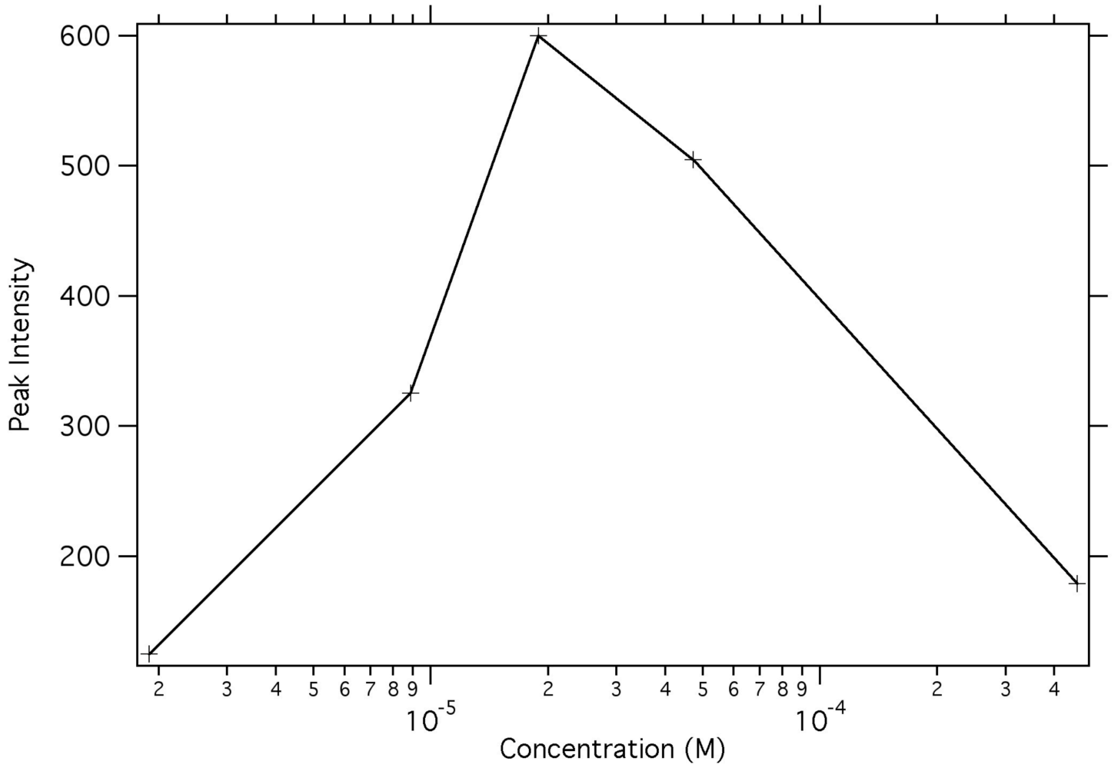

Fig. 9. The value of the emission intensity peak as a function of concentration for Rhodamine.

Figure 10 shows the normalized luminescent intensity and the absorbtance of the $2x10^{-5}$ M concentration of Rhodamine. There is a large amount of overlap between the absorption spectrum and the emission spectrum. A large portion of the light emitted will be reabsorbed, which is undesirable for an LSC. Taking the difference of the emission and absorption peaks, this gives a Stokes shift of 43 nm. A dye should have a larger Stokes shift to make a good candidate for an LSC to minimize self absorption. Fortunately, Rhodamine's high quantum yield makes it worth investigating further for use as an LSC.

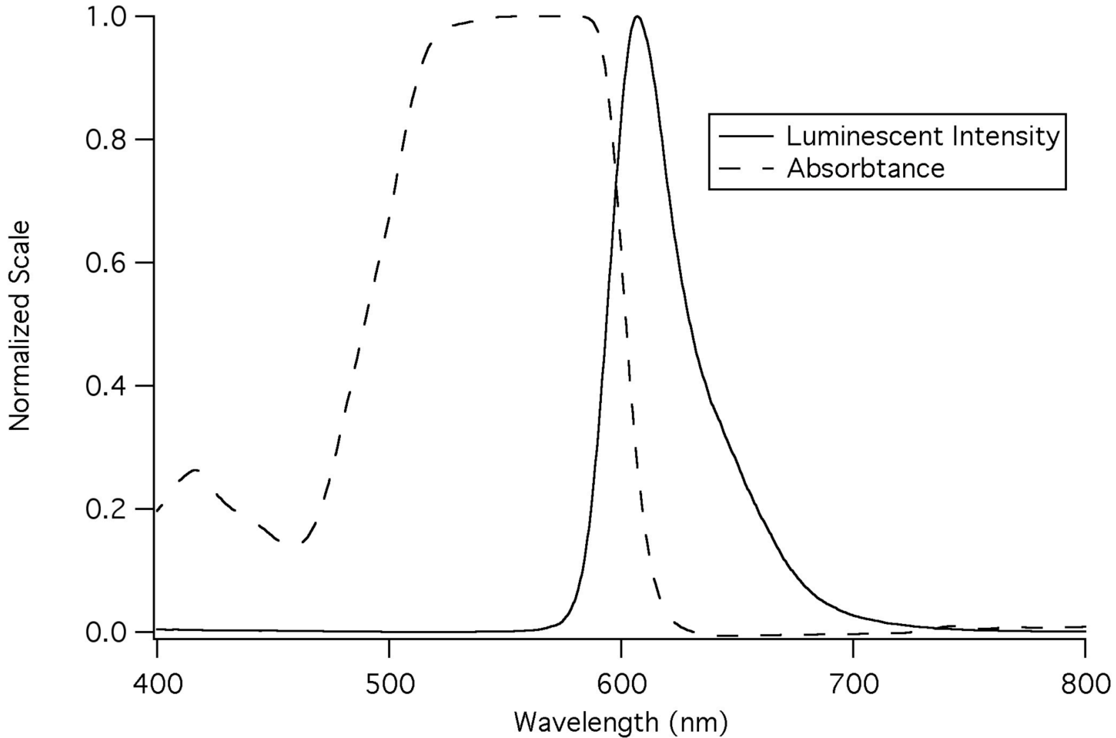

Fig 10. Normalized luminescent intensity and absorbtance of $2x10^{-5}$ M Rhodamine.

For the next set of scans, absorption and emission spectra Rhodamine, RP 231, and Red O were measured. The 0.001 % by mass (2x10-5 M) concentration sample of Rhodamine was used as the standard. The excitation intensity at 505 nm was measured by placing a white diffuse scatterer in the sample holder of the fluorescence spectrometer. The absorbtance and emission intensity data are displayed in figures 11 and 12.

The absorbtance for all three dyes should be near zero for wavelengths above 650 nm. Figure 11 shows otherwise, and in fact, Rhodamine is shown to have a negative absorbtance. The discrepancy was caused by the sample cuvettes being either cleaner or dirtier than the cuvette used for the baseline scan. This could have been avoided if more care had been taken to keep the conditions of the cuvettes consistent while scanning.

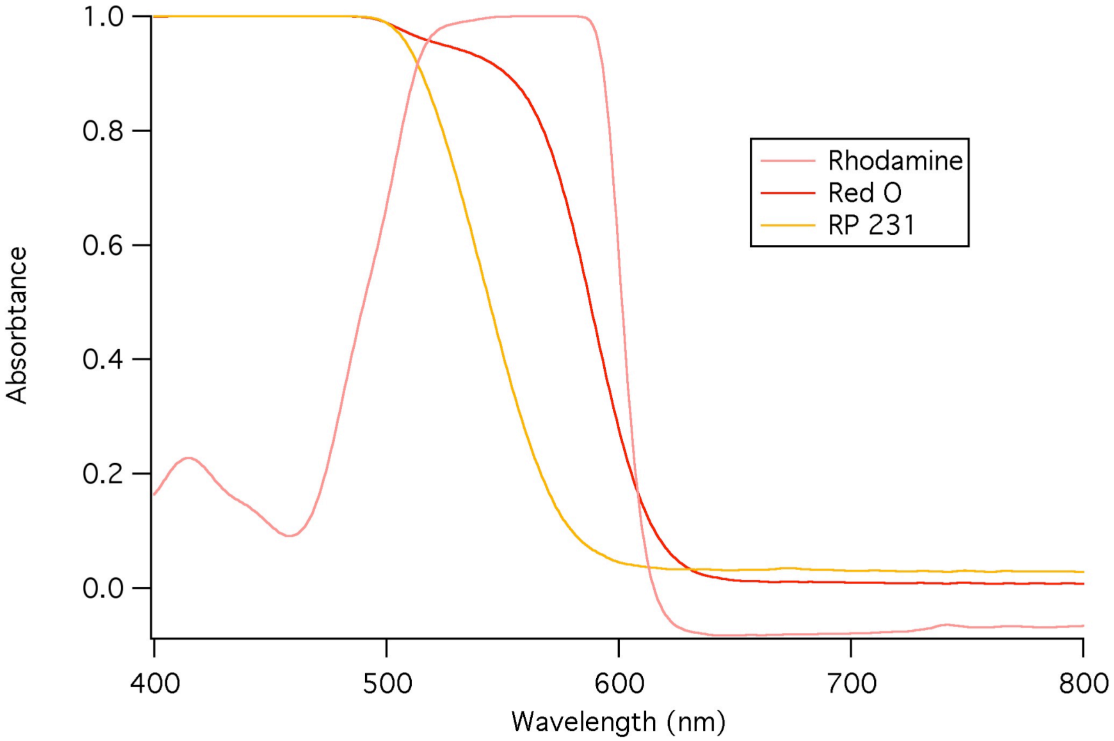

Fig. 11. The calculated absorbtance as a function of wavelength

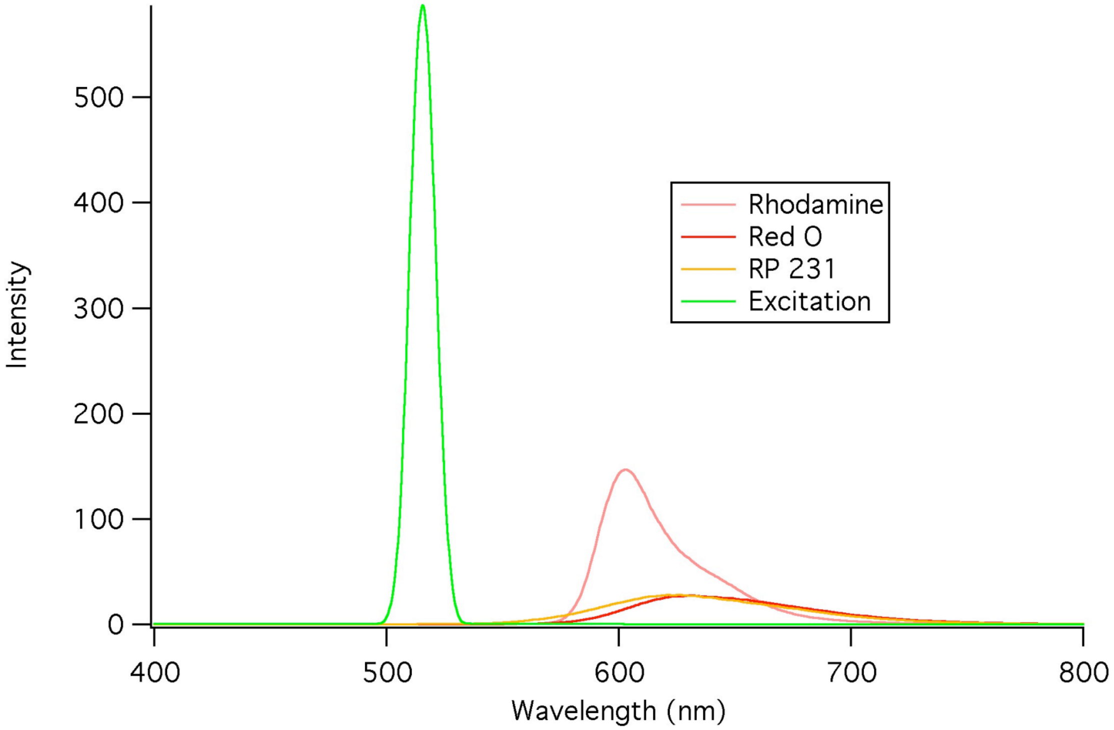

Fig. 12. The photoluminescent intensity of several dyes and the intensity of the excitation light.

Figures 13 and 14 show the normalized luminescent intensity and absorbtance of the dyes RP 231 and Red O. There is far less overlap for RP 231 and Red O than seen for Rhodamine. There is slightly more overlap for Red O than for RP 231. If the peak of the absorbtance of RP 231 and Red O are both around 500 nm and the peaks of the emission are at 624 and 632 nm respectively, then the dyes have a Stokes shift of around 124 and 132 nm. Even though Red O has a larger Stokes shift than RP 231, Red O has more overlap. This is because RP 231 has a steep drop in absorbtance, but Red O has a shallower drop. Both dyes have good relation between the absorption and emission spectrum. This is necessary, but not sufficient to make a good LSC. Another important factor is the quantum yield of the dyes.

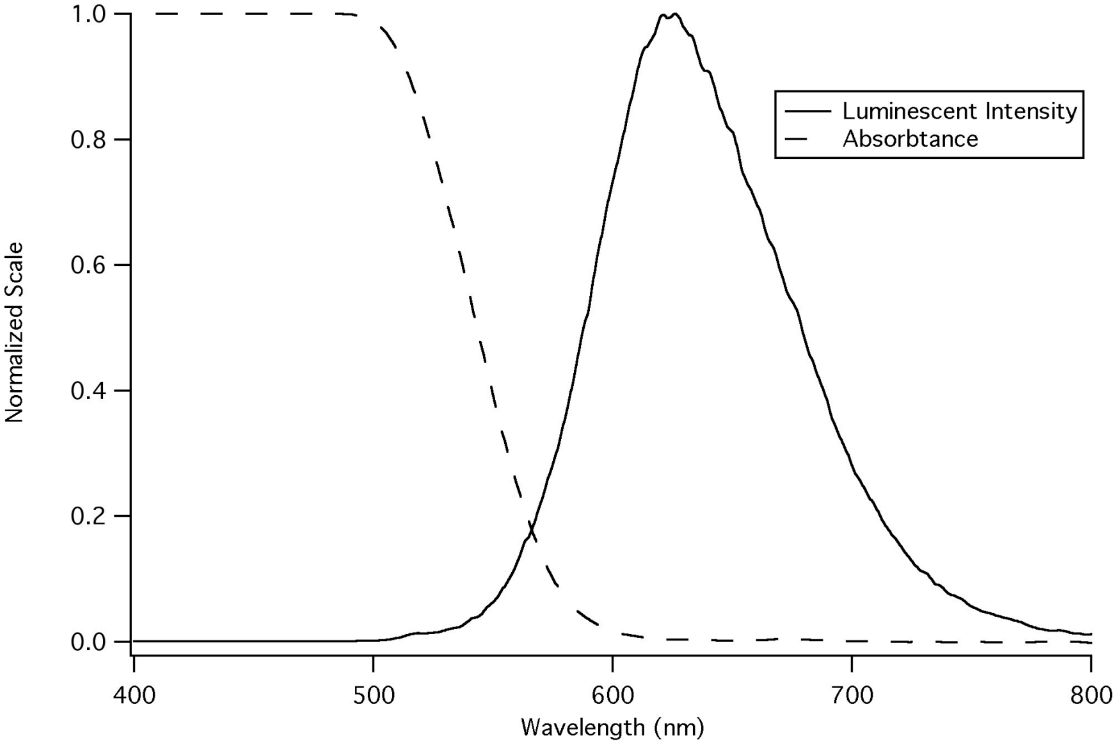

Fig. 13. Normalized luminescent intensity and absorbtance for RP 231.

To calculate the quantum yield, recall equation 9. The value φ and the relevant quantities needed to calculate it for RP 231 and Red O are listed in table 3. Fortunately, it is unlikely that the cleanliness of the cuvettes posed a problem to the quantum yield calculations for Red O and RP 231. This is because the absorbtance around the wavelength of the excitation light is much closer to unity than zero. The cleanliness of the cuvettes has a much larger effect on wavelengths with high transmittance because light blocked by dust or oil on the cuvette is negligible compared to light blocked by dye for wavelengths near the peak of the absorbtance of the dye.

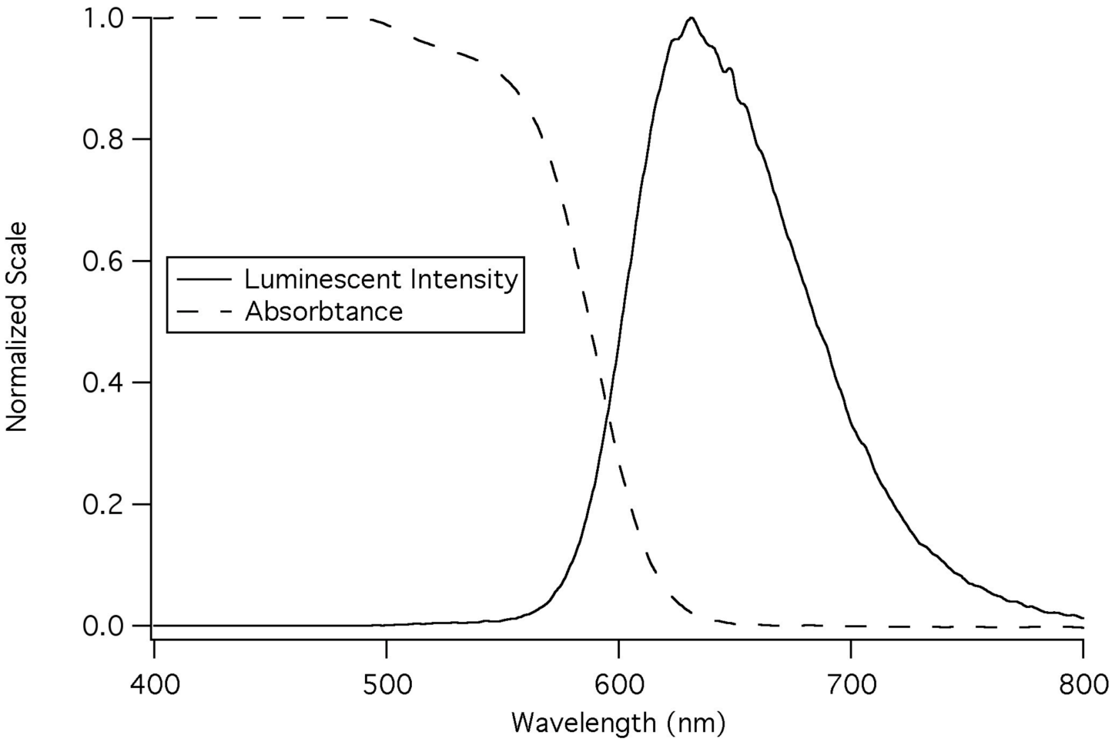

Fig. 14. Normalized luminescent intensity and absorbtance for Red O.

After the results for the RP 231 and the Red O were calculated, it was discovered that the dyes need to have low optical density. This should have resulted in inaccurate quantum yields. However, the values are comparable to those taken by colleagues using proper concentrations. It is possible that the variation in the fraction of light emitted compared to the light absorbed for the samples was cancelled by a similar variation in the Rhodamine standard. Other likely reasons for the comparable quantum yield values are the large Stokes shifts for Red O and RP 231. The wavelengths of the absorption and emission peaks of Red O and the RP 231 are highly separated, so it is unlikely that self absorption will be large. The self absorption is the primary reason to measure the values at low concentrations.

Quantum yields of about a half, such as RP 231 can make sufficient LSCs. If about half the photons absorbed are reemitted, and then three quarters of the reemitted light is trapped by total internal reflection, over a third of the incident light can make it to the photovoltaic cells on the edge. Considering the light is being concentrated to a smaller area of a solar cell, a third of the original light can still lead to a net gain in efficiency for the cell. It is likely that RP 231 would make a better quality LSC than Red O because its quantum yield is larger, and there is less overlap for it absorbance and emission intensity spectra. However, both dyes show potential, and should be further explored as LSC candidates.

Dye	$\int I_{em} d\lambda$	$\int I_{ex} A d\lambda$	*n (of solvent)*	φ
Rhodamine (0.001 % by mass)	13000	15000	1.36	1
RP 231	5500	14000	1.5	0.53
Red O	5000	16000	1.5	0.45
Rhodamine ($3x10^{-5}$ % by mass)	1750	360	1.36	1
Red F	800	980	1.5	0.21
Grand Red	360	320	1.5	0.22
Arkansas Violet	310	660	1.5	0.12

Table 3. The integrated emission intensity, the integrated absorbed excitation intensity, the index of refraction of the solvent, and the calculated quantum yield for various dyes.

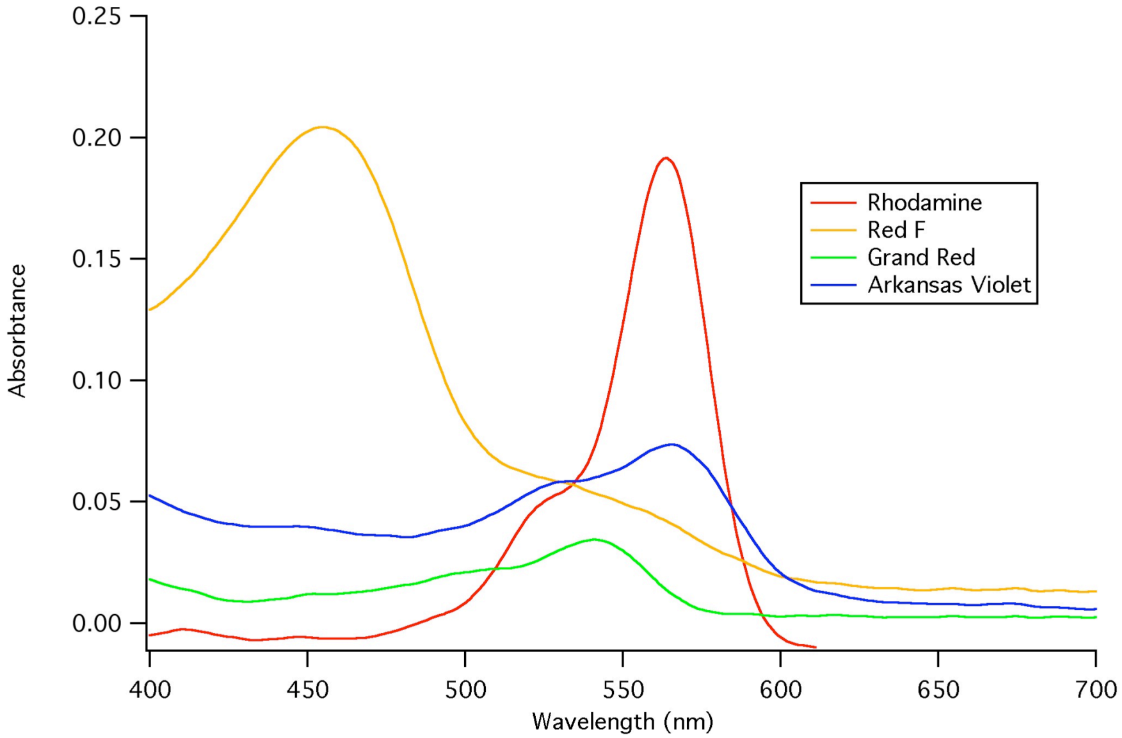

Fig. 15. The calculated absorbtance for four different dyes as function of wavelength.

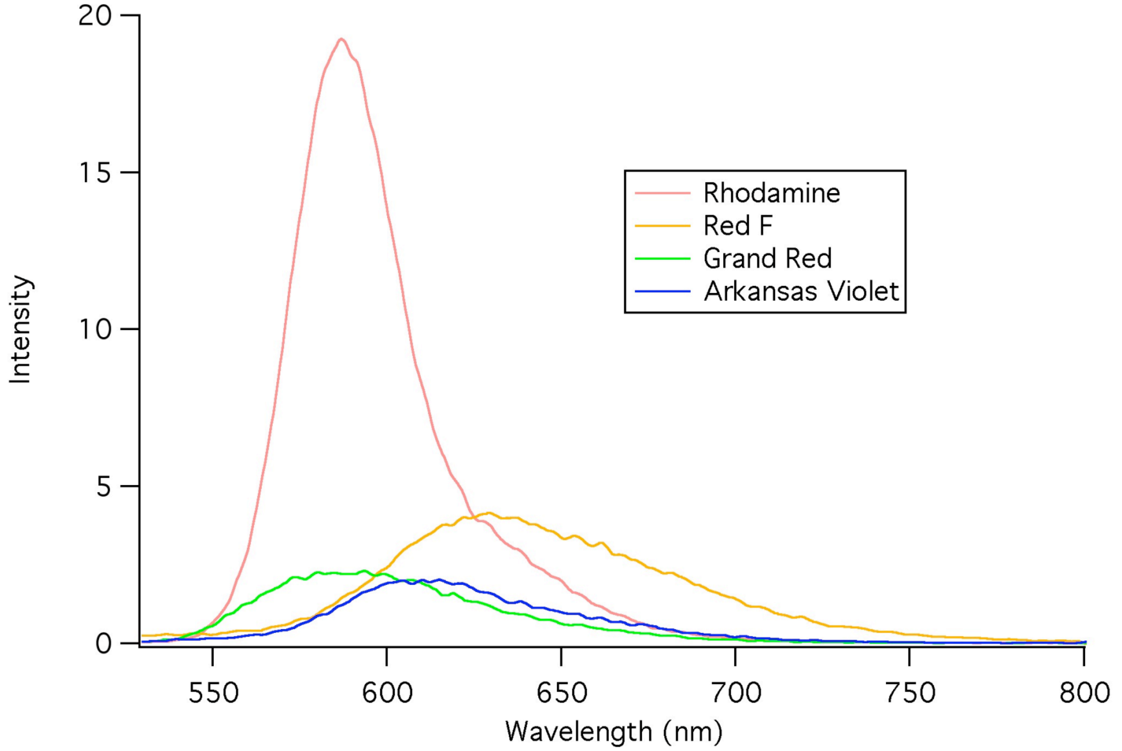

Fig. 16. The photoluminescent intensity as a function of wavelength. The dyes were excited with a 505 nm excitation wavelength.

For the second set of quantum yield measurements, absorption and emission spectra of Rhodamine, Red F, Grand Red, and Arkansas Violet were measured. The sample of Rhodamine with a concentration of 3×10^{-5} % by mass was used as a standard. The excitation curve was the same as the previous method. The absorbtance and fluorescent intensities are shown in figures 15 and 16.

The relevant quantities and the calculated values for the quantum yield for Red F, Grand Red, and Arkansas Violet are also displayed in table 3. The value of φ is likely too small for Red F, which should be 0.67. [14] Although the absorbtance at the peak excitation wavelength (505 nm) for Rhodamine is less than 0.1, at longer wavelengths, it is significantly higher. Since the absorbtance of the standard is too high, the quantum yields of Red F, Grand Red, and Arkansas Violet will be recalculated using the method of measuring quantum yield described with equation 10.

The emission intensity curve and the absorbance for Arkansas Violet are plotted in figures 17 and 18. There is more statistical variation in the luminescent intensity scans than in previous scans. This is caused small luminescent intensities at the low concentrations. With fewer photons being counted, a small variation in the expected smooth emission curve will be more noticeable. The tails of the absorbance of Arkansas Violet match much more closely to axis line than many of the previous scans. This is because more care was taken with the cleanliness of the cuvettes while handling them. The absorbance and emission intensity curves for Rhodamine, Red F, and Grand Red are not shown. However, the integrated intensity is plotted against the absorbance for each of the dyes in figures 19-22. The slopes of the linear approximations in figures 19-22, the indices of refraction of the solvents, and the quantum yields are listed in table 4.

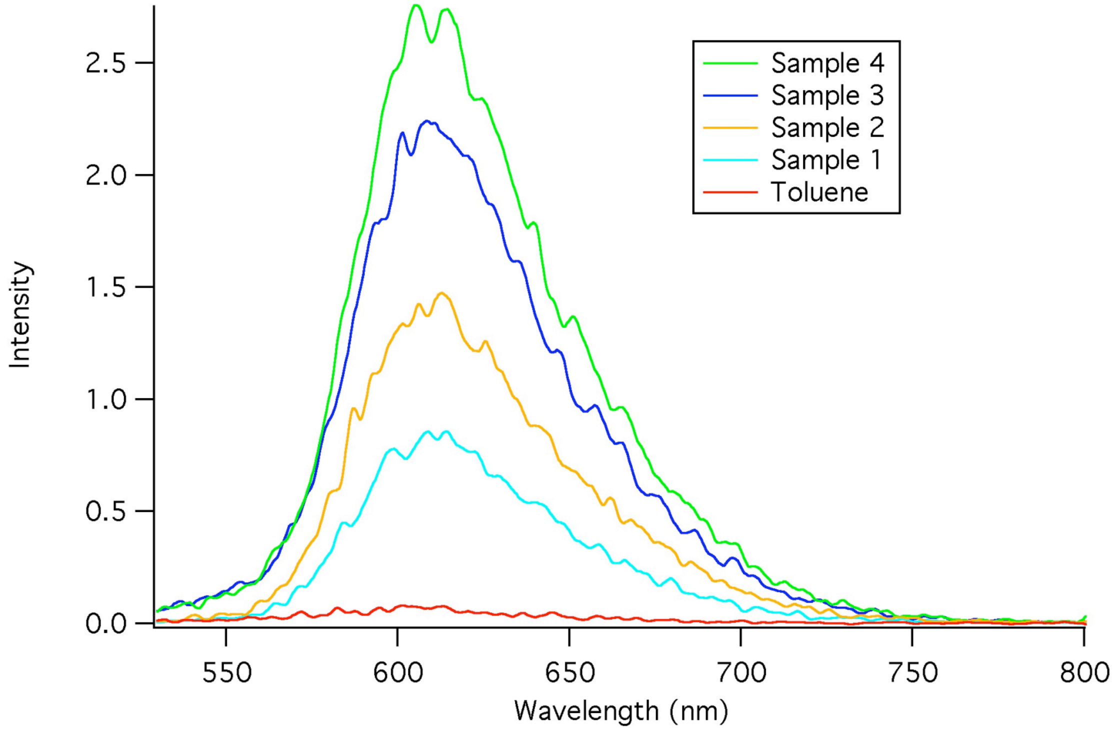

Fig. 17 Measured photoluminescent intensity of Arkansas Violet for concentrations near $4x10^{-4}$ % by mass.

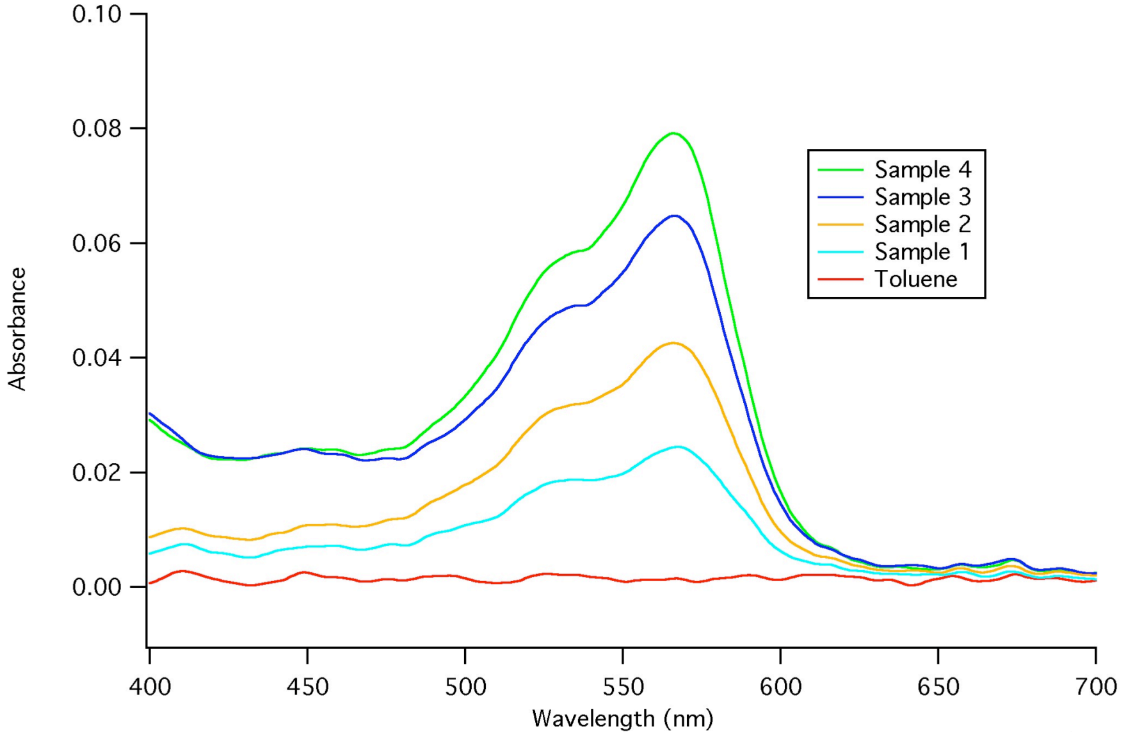

Fig. 18. Calculated absorbance of Arkansas Violet for concentrations near $4x10^{-4}$ % by mass.

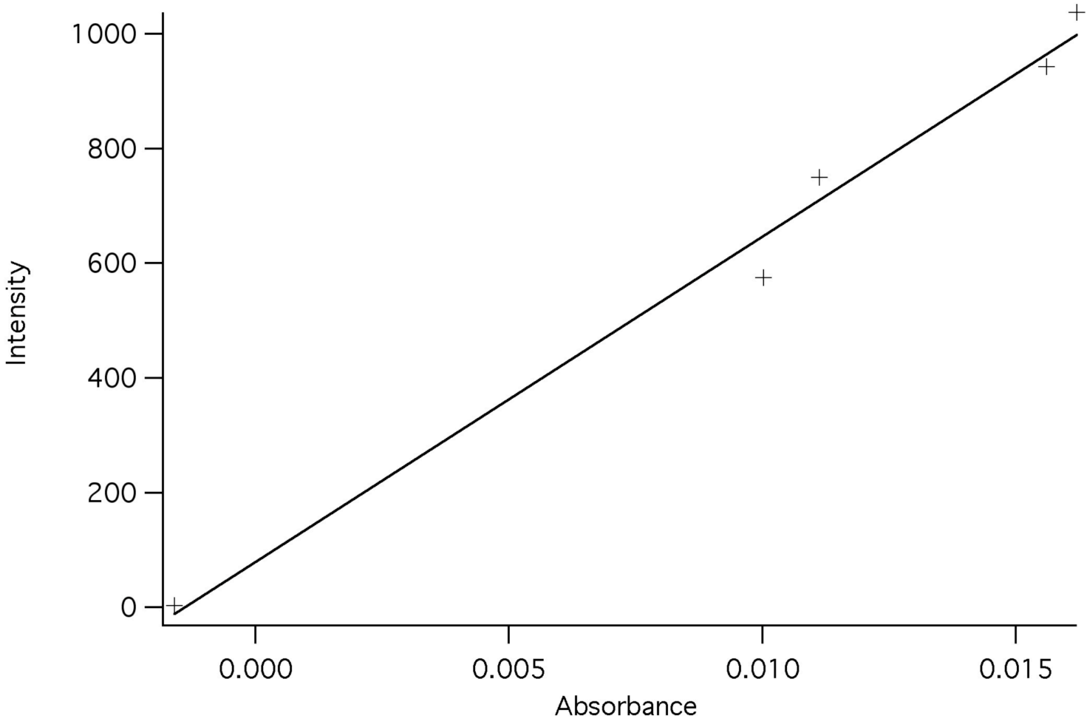

Fig. 19. Integrated photoluminescent intensity vs. absorbance as concentration of Rhodamine varies.

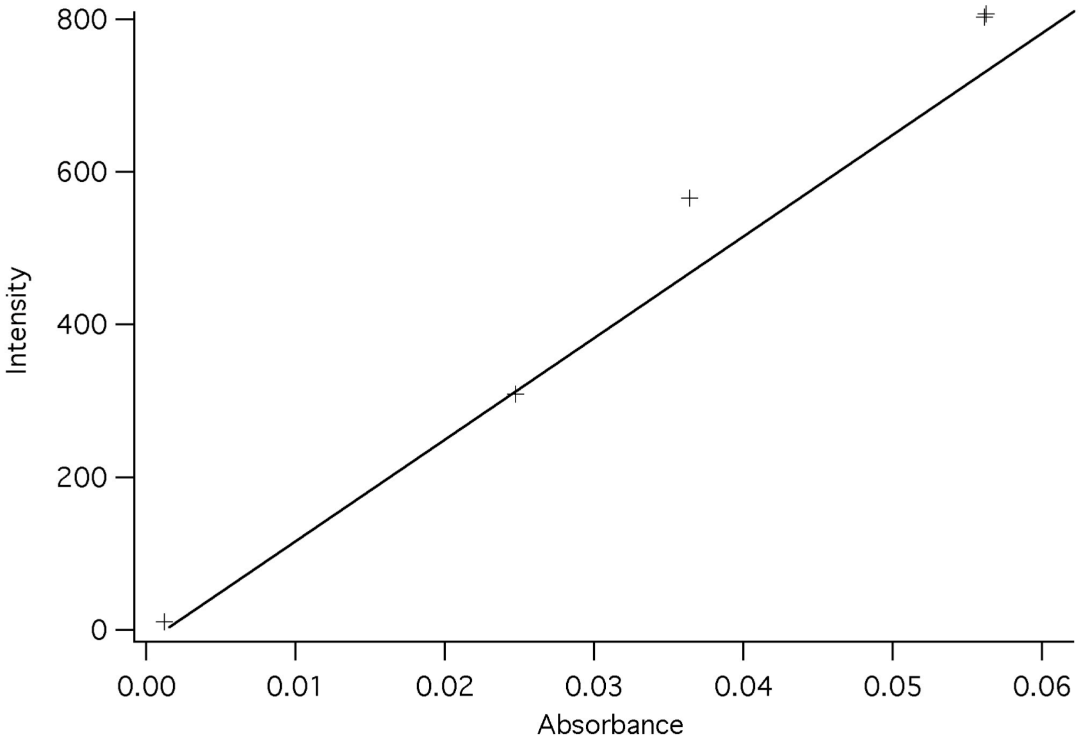

Fig. 20. Integrated photoluminescent intensity vs. absorbance as concentration of Red F varies.

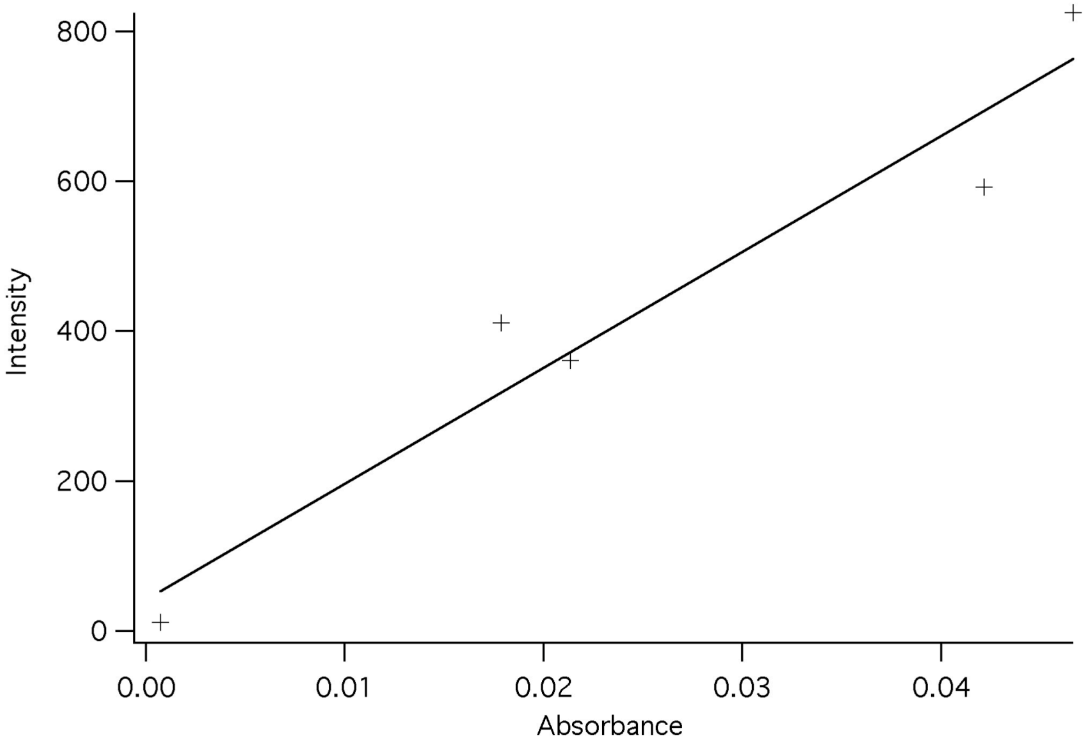

Fig. 21. Integrated photoluminescent intensity vs. absorbance as concentration of Grand Red varies.

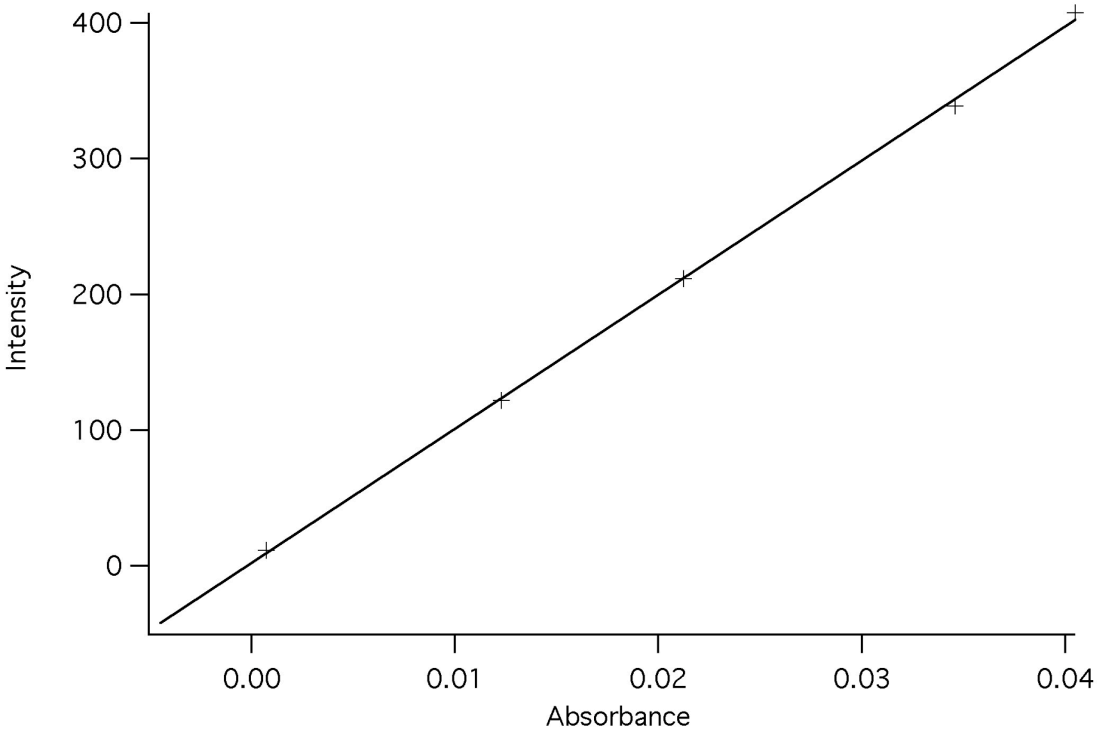

Fig. 22. Integrated photoluminescent intensity vs. absorbance as concentration of Arkansas Violet varies.

Dye	b	n (of solvent)	φ
Rhodamine	56700	1.36	1
Red F	14700	1.5	0.31
Grand Red	15500	1.5	0.33
Arkansas Violet	9900	1.5	0.21

Table 4. Slope of the linear approximation of the integrated intensity vs. the absorbance, index of refraction, and quantum yield for each dye.

Unfortunately, the quantum yield for Red F is still smaller than expected. The degradation of the value for Red F is likely caused by exposure to the air. The sample crystals are about four or five years old, and they have been stored in the air. During this time, many of the molecules have probably oxidized, and are no longer able to fluoresce.

Quantum yields of 0.2 to 0.3 are probably too low to use in an LSC. Considering the emitted light lost out of the light cone, at most, about 15-20% of the light that entered the LSC would make it to the solar cells. This is not even taking into account potential losses from self absorption. For a viable LSC, it is likely that a dye with a quantum yield of at least 0.5 would be necessary. With the right geometry, a concentrator could get a net increase in efficiency with a quantum yield of 0.3, but it would be more practical to work with as high a quantum yield as possible.

Assuming Red F does have a quantum yield of 0.67, its absorption and emission spectra need to be examined in order to judge whether or not it would make a favorable LSC. Figure 23 shows the normalized absorbance and luminescent emission spectra. The measured Stokes shift for Red F is 175 nm. This is even larger than RP 231 and Red O. However, the tail of the absorption curve goes out far from the peak, so some amount of self absorption is going on in the 500-600 nm. Fortunately, most of the emitted light can make it through without being absorbed.

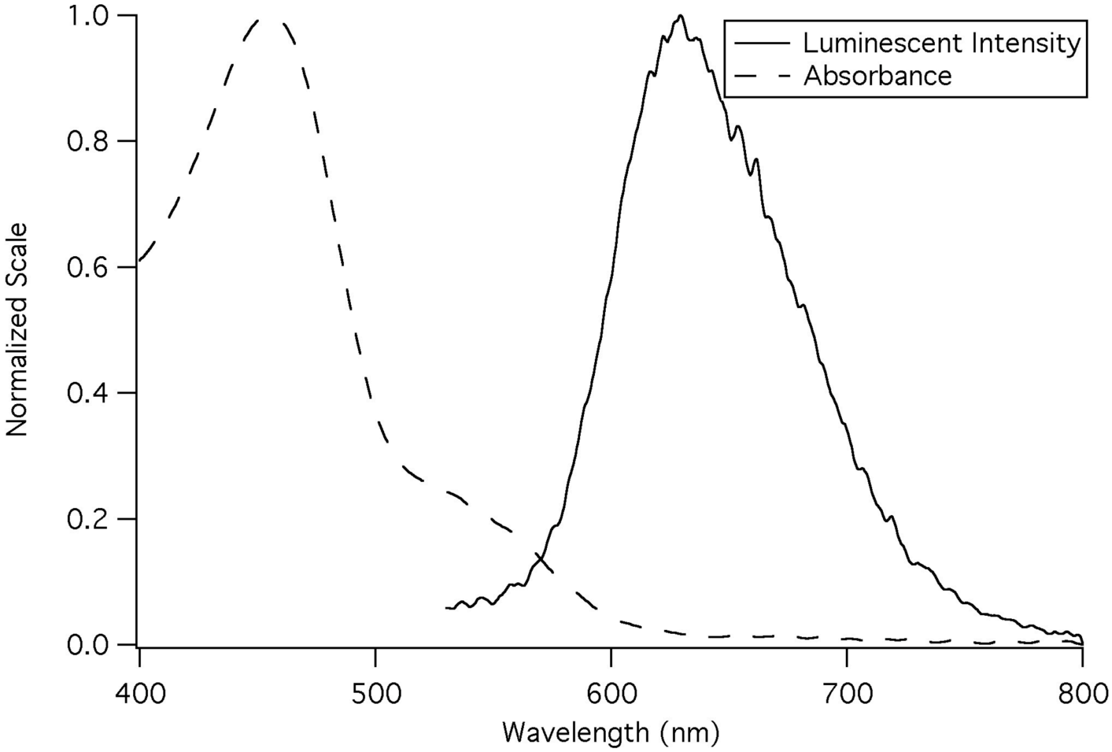

Fig. 23. Normalized luminescent intensity and absorbance for Red F.

Conclusion

Despite the high overlap of absorption and emission for Rhodamine 101, the high quantum yield makes it a possible candidate for use in a luminescent solar concentrator. Grand Red and Arkansas Violet both have a quantum yield too low to use in an effective LSC. Red F, Red O and RP 231 all have a large Stokes shift, meaning there will be comparatively little self absorption. Additionally, they have quantum yields high enough to make a potentially successful LSC. Further investigation should be done on Rhodamine, Red F, RP 231, and Red O. If it is shown that they can be made into viable LSCs, a cheaper alternative to current solar power generation may be approaching.

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