

Implementation of a Comparative Method for Measuring Photoluminescence Quantum Yields of Novel Compounds in Solution

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2016

Abstract

Quantum yield is an important, characteristic quantity to be measured for fluorescent compounds. Here, a comparative method between fluorescent compounds in solution is applied to measure unknown quantum yields. An absorption spectrometer was used to measure the absorbances of two different fluorescent quantum yield standards. The integrated fluorescence intensities were obtained using a double monochromator and plotted against the corresponding absorbances, resulting in two calibration curves. The fluorescence quantum yields of cresyl violet and fluorescein calculated via these curves were 0.55 ± 0.02 and 0.77 ± 0.01 , respectively. These are within 2.7% and 2.9% of their respective literature values. The quantum yields of zinc-oxide(ZnO) microspheres and Anthradithiophene-triethylsilylethynyl-fluorine(ADT-TES-F) in solution were also measured. The results for the ZnO microspheres were inconclusive, but the ADT-TES-F trial gave a fluorescence quantum yield of 0.44. The implementation of this method allows for the easy measurement of quantum yields with reasonable accuracy in the future.

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Chapter 1 – Introduction

1.1 Overview of Quantum Yield

Quantum yield is defined as the ratio of photons emitted by a molecule to the photons absorbed by that molecule. It is an important property to ascertain in most every material.

$$\Phi = \frac{\text{Number of photons emitted}}{\text{Number of photons absorbed}} \quad (1)$$

It can also be represented by the recombination rates of the radiative and non-radiative relaxation pathways that the electrons use to traverse back down to the ground state:

$$\Phi = \frac{K_R}{K_R + \sum K_{NR}} \quad (2)$$

Where K_R is the relative rate of the radiative relaxation pathways, K_{NR} is the relative rate of any non-radiative relaxation pathways, and the summation is over all non-radiative pathways.

When a molecule is excited by a photon of sufficient energy, an electron is excited to a higher electronic state in that molecule. The electron will not reside in this excited state for long, usually only on the order of tens of nanoseconds[1]. After such time has passed, the energy is either lost entirely to some internal source, such as vibrational energy or thermal energy, or a photon is re-emitted as the electron returns to the ground state. This re-emission process is called fluorescence. The re-emitted photon will be of a longer wavelength (lower energy) than the excitation photon, as there will always be some loss of energy to vibrational modes after excitation. The excitation and re-emission (or relaxation) process is shown in Figure 1.1.

This paper reports the investigation of quantum yield by a comparative method outlined by Williams *et al.*[2] in order to establish a working, accurate method of measuring quantum yield.

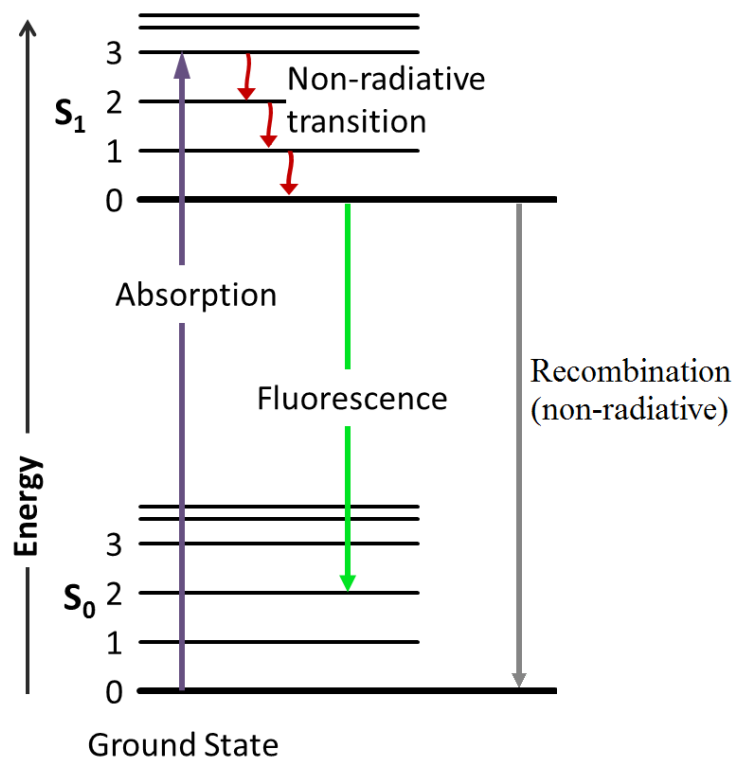


Figure 1.1 – A Jablonski diagram depicting the absorption of a photon of some energy, hf_1 , exciting an electron in the ground state of some molecule to an excited state. The electron will most likely not be re-emitted right away, going through a number of non-radiative transitions to slightly lower states. The electron then returns to the ground state, the compound emitting a photon of lower energy, hf_2 .

In this paper, quantum yields of standard samples of known yield in solution will be investigated using a comparative method outlined by Williams *et al.*[2] in order to establish a working, accurate method of measuring quantum yield.

1.2 Importance of Quantum Yield in Modern Science

Quantum yield is an intrinsic property of all compounds; a quantity that scientists strive to determine for any new compound or material right away. Specifically, quantum yield is a very useful quantity to know for biologists and biochemists interested in the emission strength of a certain compound. More specifically, biologists use fluorophores, chemicals that re-emit light following excitation, in many ways. Fluorophores can be used to tag certain structures on cells, or cells themselves, allowing the observer to track and observe that particular cell or cell structure. A recent experiment by de Messieres *et al.*[3] demonstrated this ability by showing that it was possible to track three different populations of lipoproteins (LDL, HDL, and VLDL) through the use of three different fluorophores to label these populations.

However, we are more interested in the implications of the quantum yield values for certain compounds

in regards to solid-state physics. A quantum yield measurement can be used to assess the possible usefulness of a compound for power generation. To look at it one way, when a photon interacts with the compound, an electron is excited (assuming the photon has enough energy to excite the electron into an excited state). The electron, however, will release this energy in a short time frame in order to return down to its lowest energy state. This energy can be released as another photon, as seen in Figure 1.1, or it could be lost as heat or through vibrational modes. If the energy is lost in these ways, the energy cannot be harnessed. The more photons re-emitted post-excitation, indicating a higher quantum yield, the less likely it is that this compound will lose energy in a non-useful way. Thus, a compound found to have a high quantum yield could potentially prove to be worth investigating for uses in photovoltaics, as the electrons excited in this way could be harvested for energy generation.

1.3 Theory

In this chapter, we explore the ideas necessary to understand why the approach works. We begin by exploring the relationship between absorbance and concentration by analyzing the Beer-Lambert law. We then analyze the theory behind the comparative solution method for finding the quantum yield of compounds in solution.

1.3.1 Beer-Lambert Law

The amount of light that a solution absorbs depends on the concentration of the solute in the solution. The Beer-Lambert law demonstrates the relationship between the concentration of solute in solution and the absorbance of that solution. A , the absorbance of the solution, is related to the ratio of the input and output intensities, I_0 and I respectively, by

$$A = \log_{10} \left(\frac{I_0}{I} \right) \quad (3)$$

However, the absorption can be expressed in another way via concentration, as mentioned before. The absorption of a solution is directly proportional to the concentration of the solute in the solution, c . It is also directly proportional to the path length, the distance the light must travel through the solution, l . A proportionality constant is included to allow for the absorbance to be equated to the concentration and the path length. It accounts for the probability of transition of an electron from one state to another. This proportionality constant, ϵ , is called the molar extinction coefficient.

$$A = \epsilon l c \quad (4)$$

This relationship showing the proportionality between concentration and absorbance will be a useful tool in determining the quantum yield of our samples.

1.3.2 Comparative Solution Method

There are a number of ways to determine the quantum yield of a sample. A measurement of absolute quantum yield can be realized through the methods of Weber *et al.*[4], who utilized the “dipolar scattering of monochromatic light from solutions of glycogen as a standard unit of quantum yield”[2], or through the calorimetric methods of Olmsted[5]. However, comparative methods are by and large the most common way of determining fluorescence quantum yields of materials. This is done through the use of Eq. 5 below:

$$\Phi_U = \Phi_K \left(\frac{A_K}{A_U} \right) \left(\frac{E_U}{E_K} \right) \left(\frac{I_K}{I_U} \right) \left(\frac{\eta_U}{\eta_K} \right)^2 \quad (5)$$

where Φ is the fluorescence quantum yield, A is the absorption, E is the integrated fluorescence intensity of the emitted light, I is the intensity of the excitation light, and η is the index of refraction of the solvent for the solution. The U subscript denotes the material treated as the unknown, while the K subscript denotes the material treated as the known standard to which the unknown is being compared.

The xenon arc lamp used in the fluorimeter to generate the excitation light does not have a uniform spectrum throughout its range of wavelengths. The light produced by the xenon arc lamp is more intense at some wavelengths and less intense at others. This discrepancy can cause issues when measuring something as delicate as quantum yield, as uniform parameters must be maintained in all areas of the experiment to obtain as accurate a measurement as possible. This is corrected for, as seen in Eq. 5, by the inclusion of the intensity of the excitation light, I . The intensity of the emitted light, E , is divided by the intensity of the excitation light, thereby normalizing our emission intensity. Eq. 5 can be simplified even more by combining the E_U and A_U terms, as their ratio is equal to the slope of the line produced by plotting the integrated fluorescence intensity as a function of absorbance. The same can be done with the E_K and A_K terms. This simplification results in

$$\Phi_U = \Phi_K \left(\frac{m_U}{m_K} \right) \left(\frac{\eta_U}{\eta_K} \right)^2 \quad (6)$$

where m_U and m_K are the slopes of the unknown and the known, respectively.

Chapter 2 – Methods

2.1 Finding Quantum Yields of Solutions

For measuring the quantum yields of samples in solution, we use a method outlined by Horiba, based on the comparative method work of Williams *et al.*[2], involving a comparison of photon counts per second between solutions of different absorbances. Though good and generally accurate, performing this method is time-consuming and sensitive. Much care was taken when carrying out this procedure as only one of many variables could be varied when performing the measurements. All other variables had to be held constant as much as possible.

For this method, we varied the absorbances (or concentrations) of the various solutions we used. We also had to take care not to make the solutions too concentrated, as the interactions between the molecules when exposed to the excitation light could contaminate the accuracy of the experiment. If the concentration is too great, then a photon that gets re-emitted by one molecule could get absorbed by yet another molecule of the compound in the solution, which, if not re-emitted by that molecule, will alter the values we measure. This could adversely affect the value of fluorescence quantum yield that we calculate. To avoid this, the maximum absorbance of the solution will be restricted to 0.1 when using 1cm cuvettes.

A Cary UV-Vis-NIR spectrophotometer was used to take the absorbance measurements, which varied between ~ 0 and ~ 0.1 . The solutions were prepared semi-concentrated (~ 0.1) and were diluted down to

lower concentrations. In addition to the absorbance scans of the solutions, it was important to be sure to take a scan of the background solvent by itself, as some (and, indeed, a significant portion at times) absorbance measured is due to the solvent and not the compound itself. This background scan is then subtracted point by point from the other scans so that the maximum absorbance peak for each scan may be ascertained.

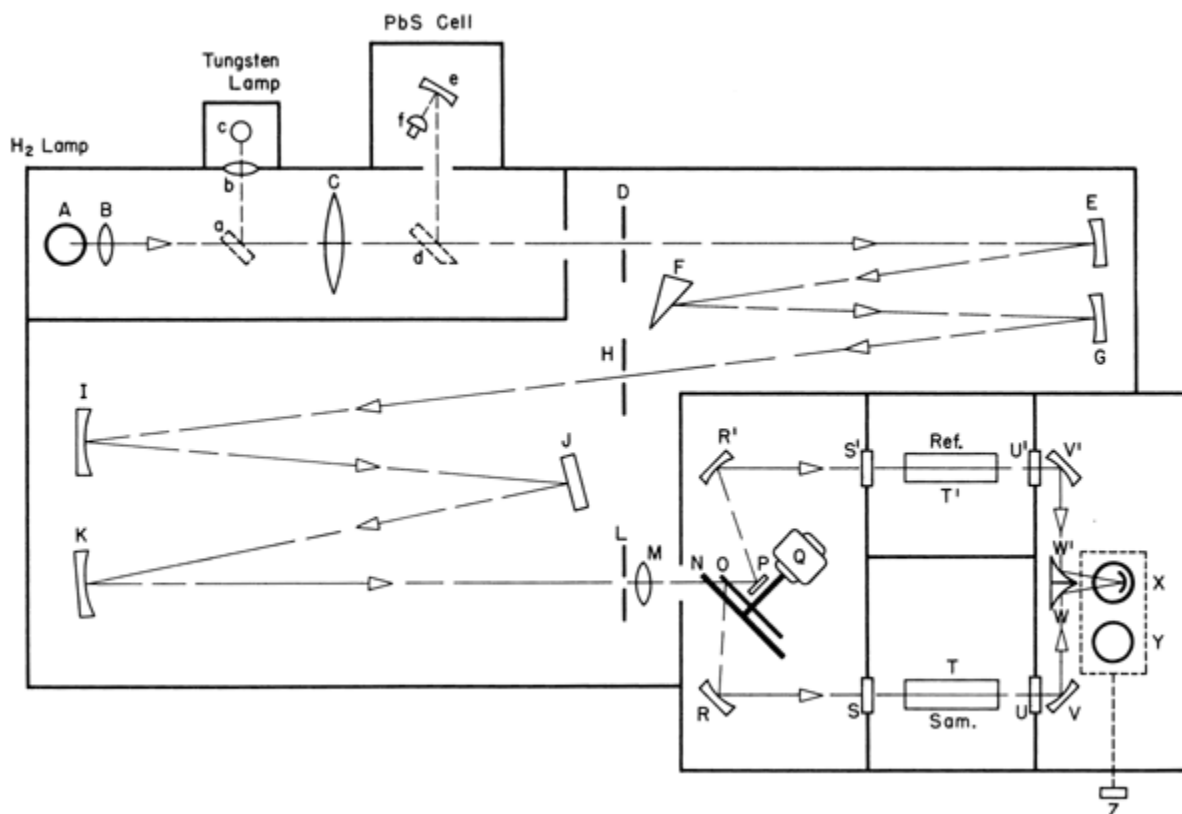


Figure 2.1 – A schematic of a spectrophotometer similar to the Cary 5 UV-Vis-NIR spectrophotometer that was used in measuring the absorbances of the samples in solution. The spectrophotometer is used to measure the intensity of light transmitted through the sample (Sam. in the figure). The spectrophotometer can also be used to measure the light transmitted through a reference sample (Ref.), allowing the machine to automatically subtract off any light-solvent interaction.

Once we have measured the absorbance of the solution in a 1-cm cuvette, we transfer this sample to the Horiba Fluorolog-3 Spectrofluorometer. The fluorimeter is then used to take an emission spectrum, using the excitation wavelength that corresponds to the wavelength where the absorbance peak measured in the absorption spectrophotometer was located. The total photon counts per second (CPS) measured over the range of emission wavelengths is then normalized by dividing the emission spectrum by the lamp spectrum. Fluorimeter measurements of the normalized photon CPS were taken in two ways, right angle (RA) and front face (FF). These two methods refer to the path of the emission light we choose to collect from the sample chamber. The RA method is the path depicted in Figure 2.2, and is generally considered to be more reliable when dealing with samples in solution. The FF method is not depicted in Figure 2.2 but differs only in the path it takes out of the sample chamber and to the emission monochromator. The light in the FF method is collected from a path anti-parallel to the light from the excitation monochromator and is generally considered better for solid-state samples.

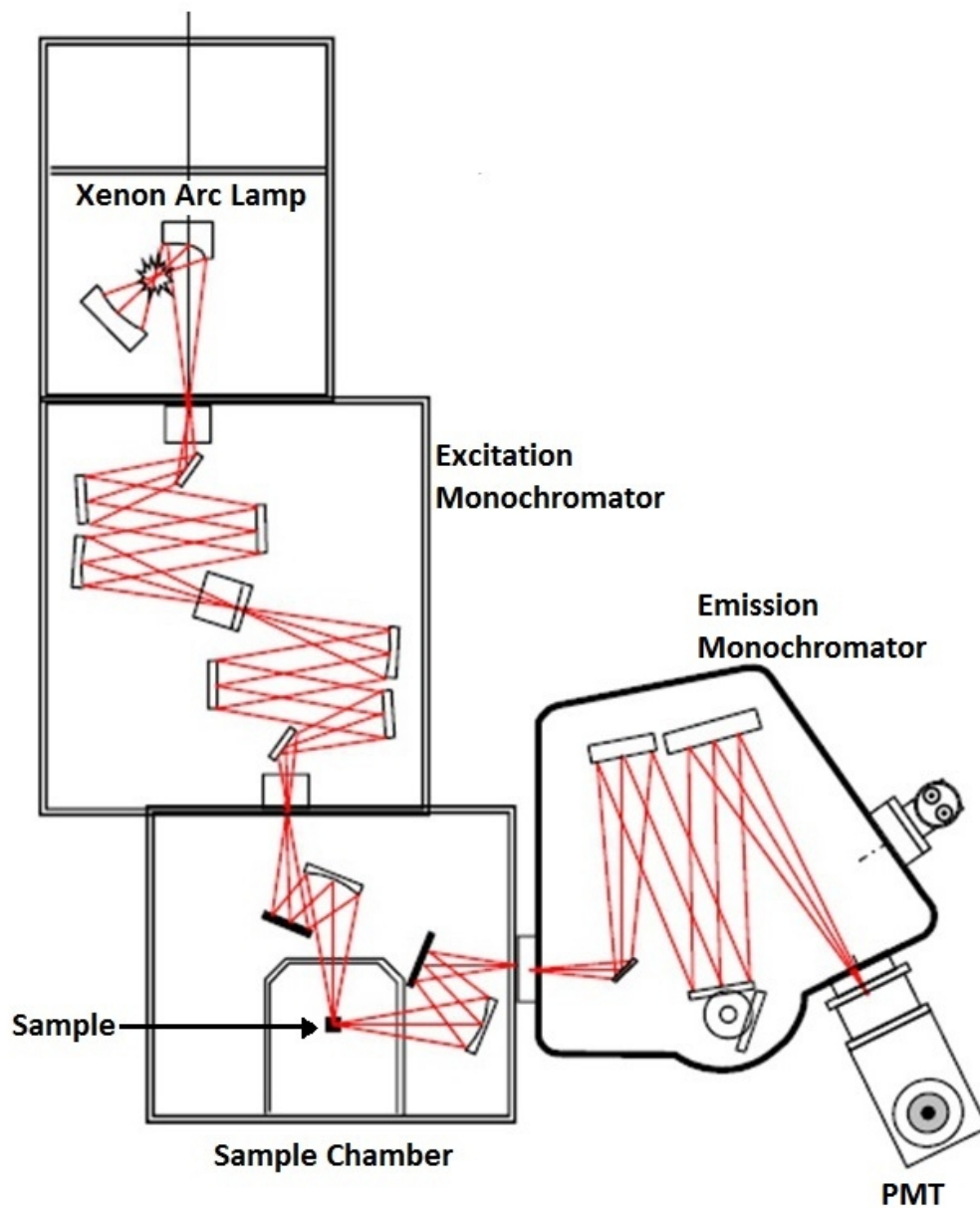


Figure 2.2 – A schematic of the Horiba Fluorolog-3 Spectrofluorometer used to determine the number of photons emitted by a sample when excited at a particular wavelength. The xenon-arc lamp produces a broad range of wavelengths of light, and the excitation monochromator selects the specific excitation wavelength(or wavelengths) desired. This light is incident on the sample, and the light emitted by the sample travels into the emission monochromator where the photomultiplier tube(PMT) detects how many photons of particular wavelength were emitted by the sample over a period of time determined by the user, referred to as the integration time.

We then find the integrated fluorescence intensity for each sample. When we have finished taking all of the emission spectra, we plot the integrated fluorescence intensity as a function of absorbance. The result should be a straight line with an intercept through the origin, as seen in Figure 2.1. We perform this process three times per quantum yield measurement: for two different standard samples in order to cross-calibrate and for the compound of unknown quantum yield.

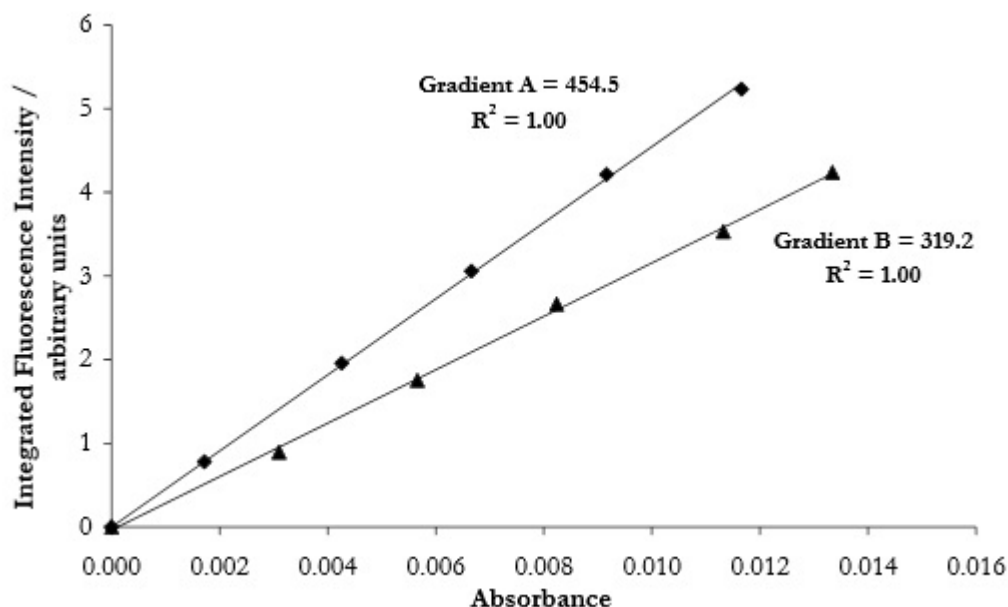


Figure 2.3 – An idealization of the expected results described in the Methods section.

Once we have the slopes for each sample, we use Eq. 2 to solve for the unknown quantum yield value, Φ_U . We do this first for the two known standard samples. If it is confirmed that the values calculated are accurate to the known quantum yields for those samples within 10%, we can proceed to calculate the quantum yield of the unknown sample, first using one standard sample's values, and then a second time with the other standard sample's values. The average of the two quantum yield value results for the unknown are then averaged, obtaining the final value for the quantum yield of the unknown sample.

For a step-by-step version of the procedure used in the experiment, see Appendix A.

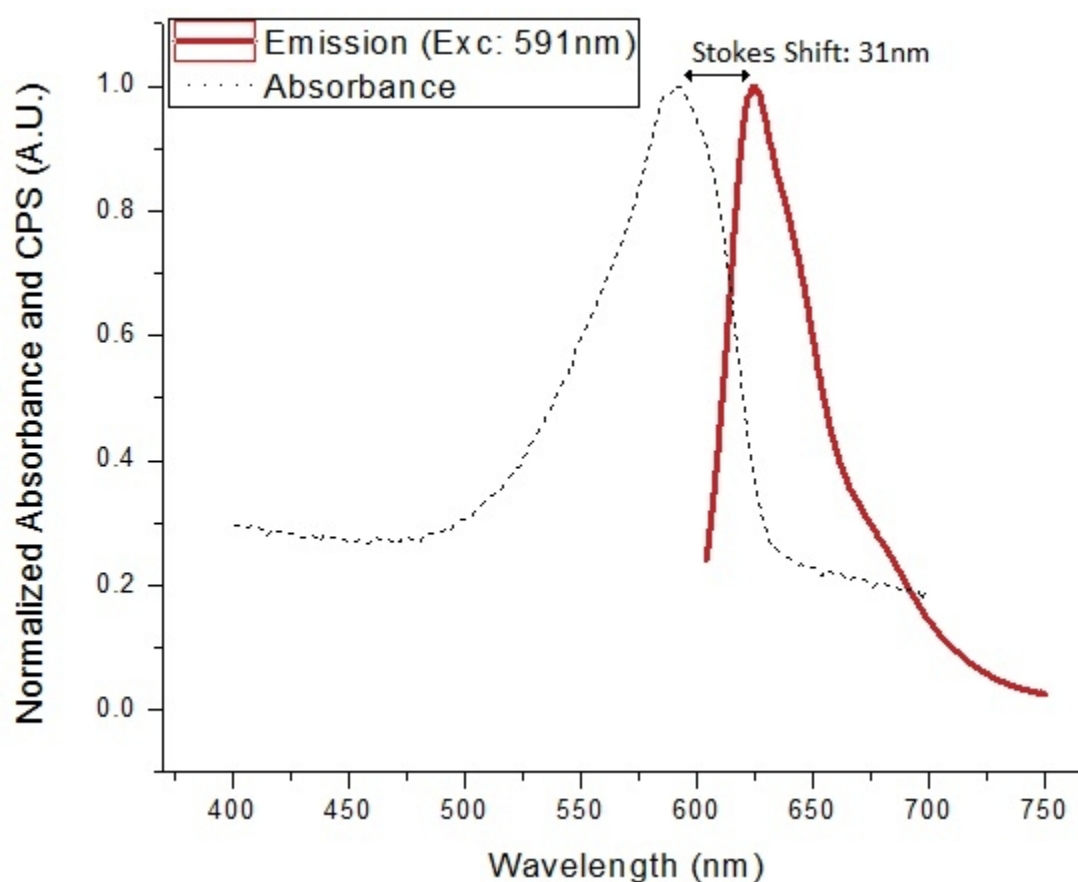


Figure 2.4 – Sample absorbance and emission spectra taken on cresyl violet. The spectra were normalized for ease of plotting.

Chapter 3 – Results

3.1 Calibration

Two trials were run for each quantum yield standard sample for the cross calibration in order to ensure a consistent and accurate method of measurement. The two quantum yield standards chosen for the calibration were cresyl violet and fluorescein.

The plots of the various trials for both cresyl violet and fluorescein can be seen below, the results of both RA measurements and FF measurements are plotted together on the same graph.

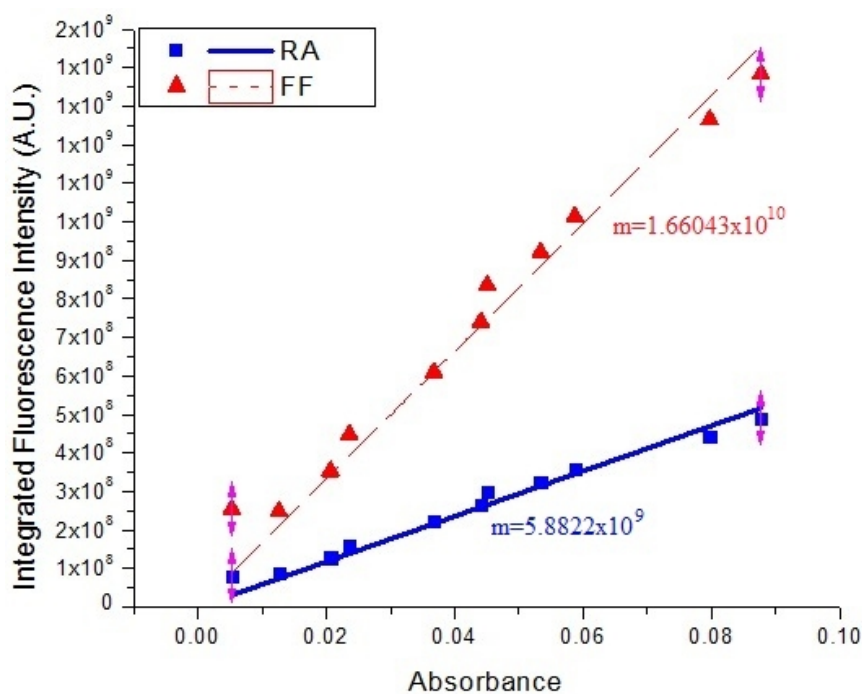


Figure 3.1 – The integrated fluorescence intensity plotted as a function of absorbance for the standard sample, cresyl violet, for both RA and FF collection methods for Trial C1.

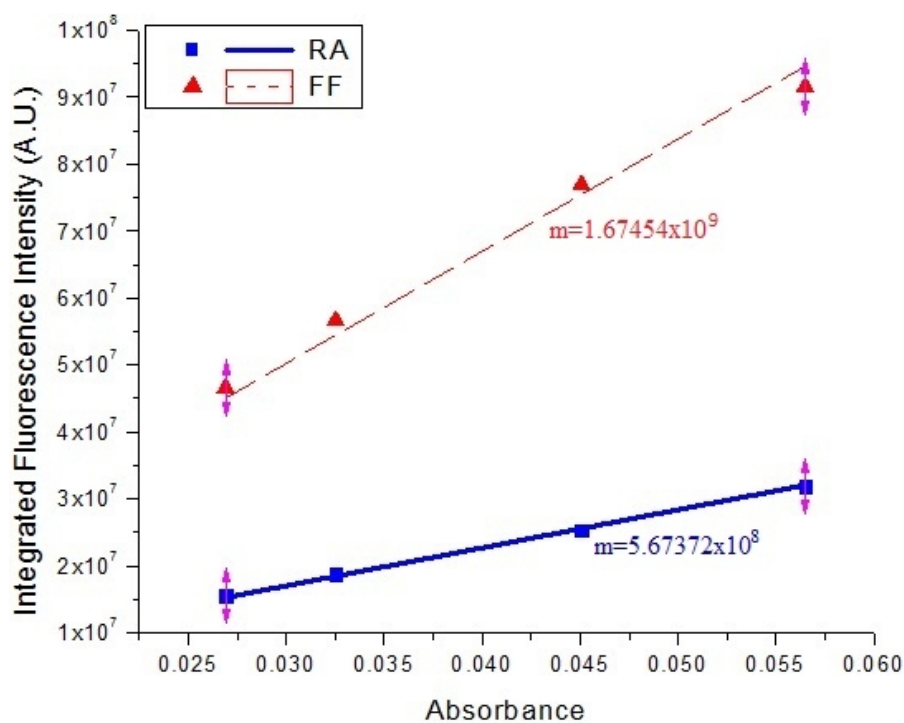


Figure 3.2 – The integrated fluorescence intensity plotted as a function of absorbance for the standard sample, cresyl violet, for both RA and FF collection methods for Trial C2.

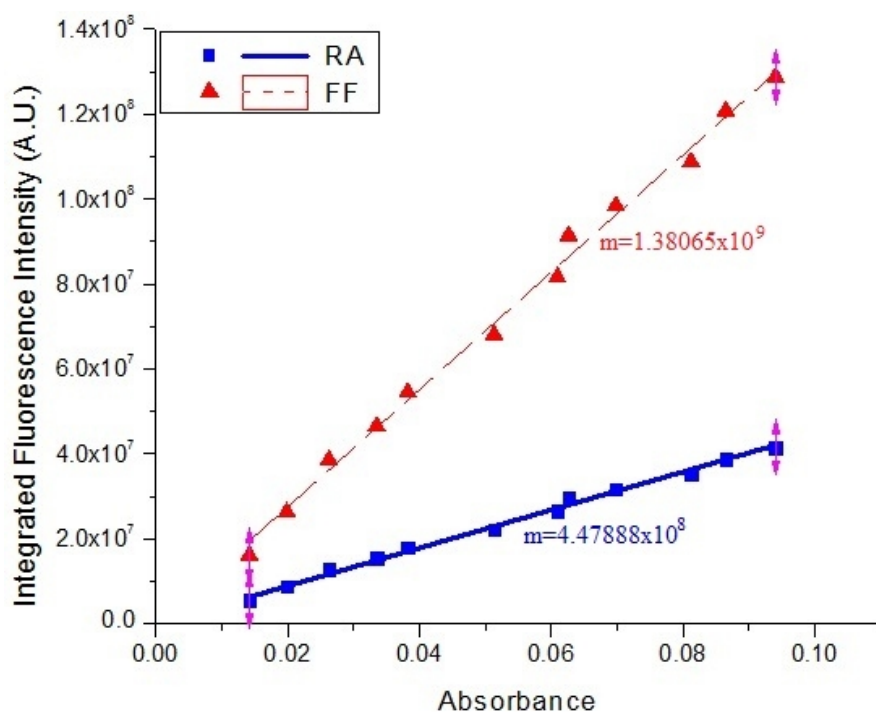


Figure 3.3 – The integrated fluorescence intensity plotted as a function of absorbance for the standard sample, fluorescein, for both RA and FF collection methods for Trial F1.

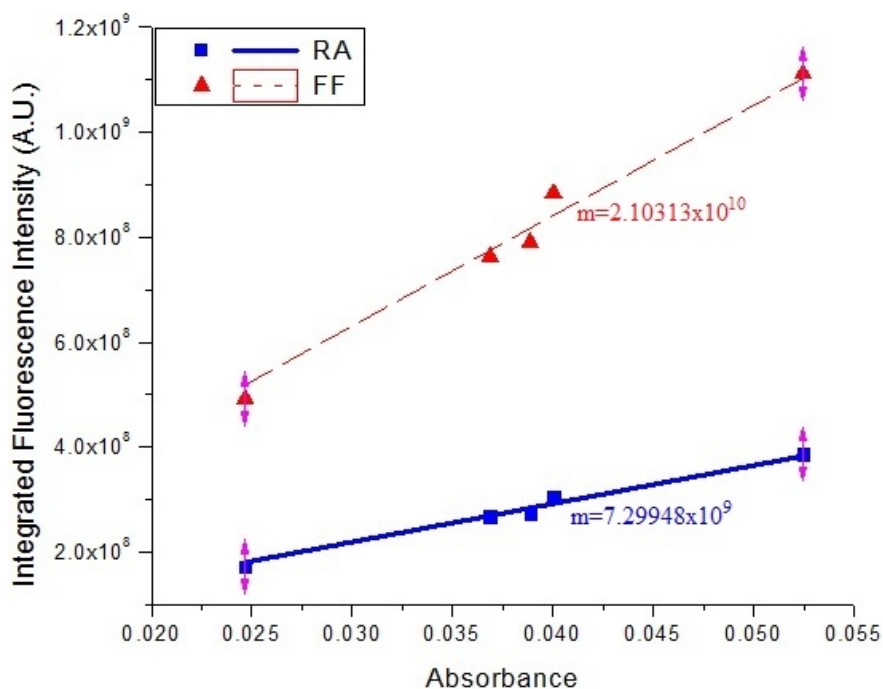


Figure 3.4 – The integrated fluorescence intensity plotted as a function of absorbance for the standard sample, fluorescein, for both RA and FF collection methods for Trial F2.

The slopes of the best fit lines were then used to calculate the quantum yields of the standard samples, first treating one as the unknown, and the other as the known, and then calculating a second time with their roles reversed. The literature quantum yield values were used for the known in all calculations.

In Table 1, the calculations are organized based on trial combination and light collection method. As there were two standards and two trials per standard, we have four combinations of calculations we can perform with the data. We are interested in which combination produces the most accurate data, as there were some slight variances in data acquisition between some of the trials which shall be elaborated on in chapter 4.

Trial Combination	C1-F1	C1-F2	C2-F1	C2-F2
RA	Cresyl QY=9.1±0.2	Cresyl QY=0.56±0.02	Cresyl QY=0.89±0.01	Cresyl QY=0.054±0.001
	Fluor. QY=0.047±0.2	Fluor. QY=0.76±0.01	Fluor. QY=0.48±0.01	Fluor. QY=7.8±0.0
FF	Cresyl QY=8.4±0.2	Cresyl QY=0.55±0.02	Cresyl QY=0.85±0.01	Cresyl QY=0.056±0.001
	Fluor. QY=0.051±0.158	Fluor. QY=0.77±0.01	Fluor. QY=0.50±0.01	Fluor. QY=7.6±0.0

Table 1 – A table summarizing the results of the quantum yield calculations for each combination of the different trials, and for both RA and FF collection methods.

The only trial combination that produced accurate yields was by using the results from trial C1 with the results from trial F2. These values differ at most by 4.9%, which is well within the 10% error threshold usually associated with the comparative method.

This method of calculation can be lengthy, so a simpler, albeit slightly less accurate, method can be used to quickly determine the QY of a compound. This method is detailed in Appendix B.

3.2 ZnO and ADT-TES-F

The unknown compounds to be measured are ZnO microspheres and ADT-TES-F. The ZnO microspheres were provided by Xiao Xia Li of the Institute of Functional Materials, and the ADT-TES-F sample was provided by Oksana Ostroverkhova of Oregon State University. The ZnO microspheres were dissolved in 0.1M NaOH, and the ADT-TES-F was dissolved in chlorobenzene. The results of both measurements can be seen in Figures 3.6 and 3.7.

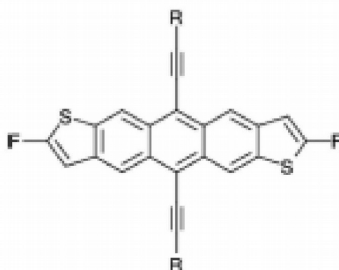


Figure 3.5 – A representation of the ADT-TES-F molecule. ADT-TES-F is a novel compound that is being studied for possible use as an organic semiconductor in organic photovoltaics.

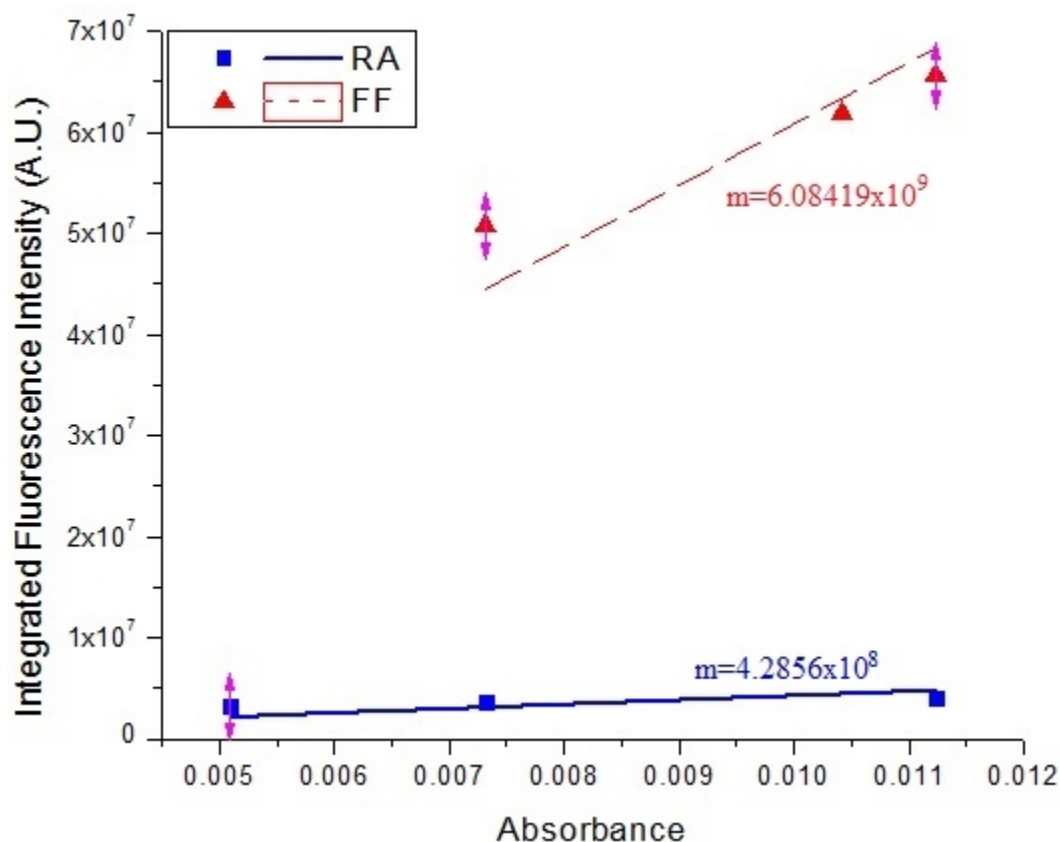


Figure 3.6 – The integrated fluorescence intensity plotted as a function of absorbance for ZnO for both RA and FF collection methods

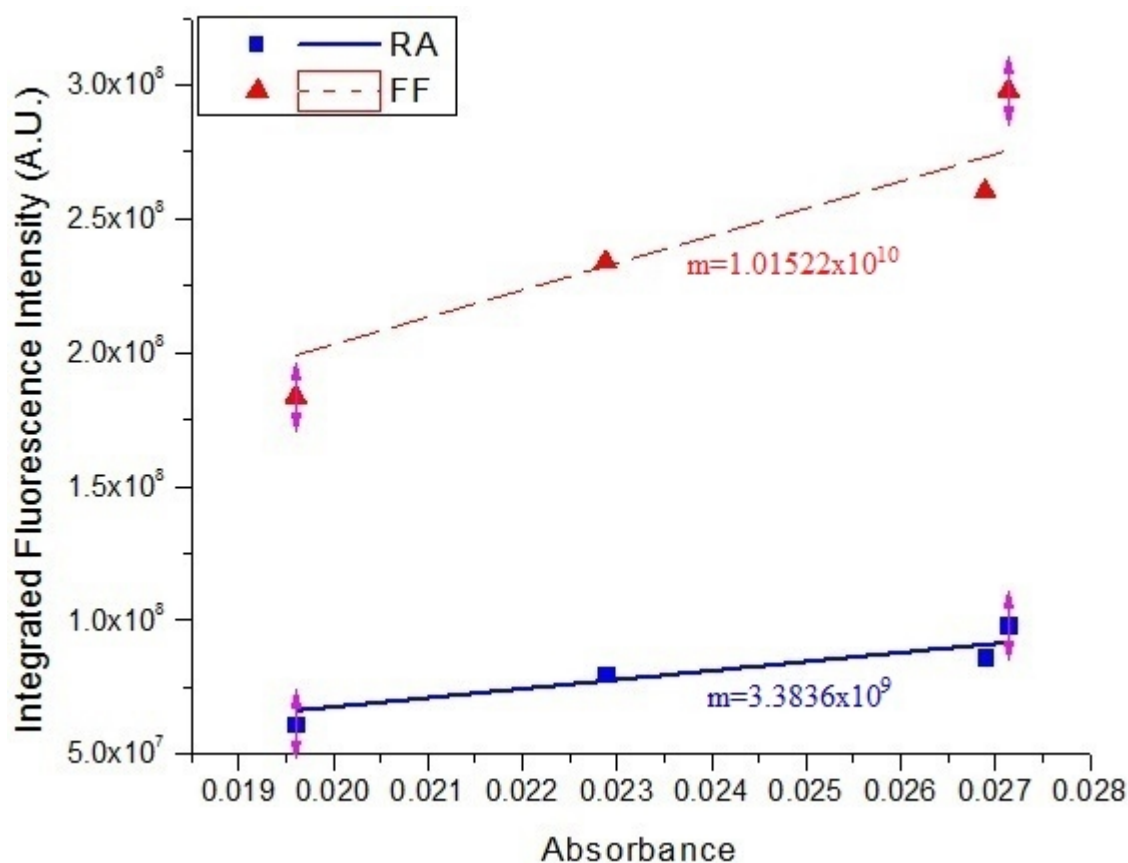


Figure 3.7 – The integrated fluorescence intensity plotted as a function of absorbance for ADT-TES-F for both RA and FF collection methods

The calculated quantum yield values for ZnO and ADT-TES-F are shown in Table 2 below. For consistency, the slopes (both for the standards and the unknowns) used for calculating the quantum yield of the unknowns were matched based on the light collection method, i.e. RA with RA, and FF with FF.

Compound	QY(ZnO)	QY(ADT-TES-F)
RA	0.042±0.005	0.42±0.01
FF	0.21±0.01	0.44±0.01

Table 2 – A table summarizing the results of the quantum yield calculations for both ZnO and ADT-TES-F for both RA and FF collection methods.

Chapter 4 – Discussion

4.1 Calibration

Before proceeding to measure the quantum yields of ZnO and ADT-TES-F, it was important that the calibration of the fluorimeter was reasonably accurate. Thus, four trials were performed, two per standard sample, in order to have an ample supply of data. Unfortunately, not enough care was taken in trials C2 and F1, as some parameters were not kept constant during the measuring of the emission spectra of the samples at various absorbances. In particular, the range of wavelengths over which the spectra were taken were different from trial C1, which was taken over a range of 43nm. The total range of wavelengths scanned through remaining constant is key to getting accurate quantum yields. This data-taking error resulted in highly inaccurate quantum yields, as seen in Table 1. The only reliable set of calculations is trial C1 with trial F2, as the above error was noticed before trial F2 was done. Trial F2 was performed using identical parameters to that of trial C1, resulting in much more favorable data.

The collection method (RA vs FF) did not seem to have a significant impact on the quantum yield values, though the FF collection method did result in slightly more accurate values. The RA collection method resulted in quantum yield values of 0.56 for cresyl violet and 0.76 for fluorescein. These values differ from their literature values of 0.54 and 0.79 by 4.8% and 4.6%, respectively. In contrast, the FF collection method values of 0.55 for cresyl violet and 0.77 for fluorescein only differed by 2.7% and 2.9%, respectively.

4.2 ZnO and ADT-TESF

As the quantum yield values in Table 2 indicate, the ZnO microspheres are orders of magnitude less fluorescent than the ADT-TES-F. However, the degree to which they are less fluorescent is more difficult to ascertain, given the large discrepancy between the results of the calculations for the RA and FF collection methods for the ZnO microspheres. Given the results from the calibration trials, even in the bad trials, there was little difference between the values acquired via RA and FF. Here, the quantum yield for the ZnO microspheres calculated from the RA collection method differs from the value via the FF collection method by 79.9%. I am unsure what happened to cause such different results between the two trials, though one possibility could be the effect of scattering. FF measurements are more reliable for when the sample causes a lot of scattering. Conversely, RA does not yield good measurements for samples with lots of scattering, as the light has to travel much farther through the sample, subjecting it to even more scattering. If this is the cause of the bad measurement, the use of a smaller cuvette and only FF measurement method would increase the accuracy and reliability of this measurement.

There is no such discrepancy in the ADT-TES-F results, as the RA results differ by only 4.93% from the FF results. As stated in chapter 4.1, the results of the calibration indicate that the FF collection method may provide slightly more accurate results, so 0.44 is likely the more accurate value of quantum yield for ADT-TES-F. There were some limitations with the ADT-TES-F sample that made data-collection slightly difficult, and that may have resulted in sub-par results. The amount of ADT-TES-F available was extremely limited, as was the amount of solvent available. Only a few data points were able to be taken, and it was limited to one trial. However, the data resulted in a roughly linear set of points, so these limitations can most likely be safely ignored. This result does, however, differ from results published by Platt *et al.*[10], where a quantum yield of ~ 0.7 was reported. This could be due to differing solvents, as the solvent used in this experiment was chlorobenzene, while Platt *et al.* used

dichloromethane. Another possibility for the differing values could be due to the quartz cuvette used in this experiment. The cuvette was not in pristine condition; it had not been cleaned as thoroughly as possible and the sides were slightly scratched.

Chapter 5 – Conclusions

A method of measuring quantum yields of samples in solution was implemented and used to determine the unknown quantum yields of compounds that had not yet been measured. The fluorimeter was calibrated successfully using two quantum yield standards, cresyl violet and fluorescein. The calibration trials indicated that both the RA and FF collection methods are valid, though the FF method provided slightly more accurate results.

With the calibration satisfactory, the quantum yields of ZnO microspheres and ADT-TES-F were measured using the comparative method. The ADT-TES-F results were reasonable; both RA and FF methods resulted in similar values. However, the RA and FF values for the ZnO microspheres were vastly different from each other, so the correct value is difficult to ascertain. Performing the same measurement using a 1-mm cuvette and FF collection method to reduce the effect of scattering may yield better results.

This method is only valid for measuring samples in solution, so future research on the implementation of a comparable method that works for thin film samples would be a logical next step. There would be some inherent difficulties with this, such as accounting for the number of layers in the sample, but it may be possible.

Acknowledgements

I would like to acknowledge my thesis advisor, Dr. Matthew W. Graham, for suggesting the project to me, and for his support and feedback throughout this work. I would also like to acknowledge the Summer Undergraduate Research Experience in Science (SURE Science) Scholarship for providing the funds that made this research possible. Additionally, I would like to acknowledge the Research Equipment Reserve Fund (RERF) for providing the necessary funds to purchase the fluorimeter.

Appendix A

A step-by-step procedure of the comparative method used in this experiment.

1. Prepare a very dilute solution using your sample and your chosen solvent. It is a good idea to use the proportionality between concentration and absorbance to determine the mass of sample and volume of solvent to use to prepare the solution, but generally the mass to be measured out is extremely small. This can make using this approach difficult. As an alternative, one can simply measure the absorbance of the prepared solution, and then dilute or increase the concentration as needed. Though not the best method, it suffices if measuring the desired mass is unfeasible.
2. The maximum absorbance of the sample allowed for this measurement depends on the size of cuvette used. If a 1-cm path-length cuvette is used, the maximum absorbance is 0.1 (Specifically, the max absorbance refers to the absorbance at the absorbance peak of the sample with the solvent absorbance subtracted off). If a 5-cm path-length cuvette is used, the maximum

absorbance is 0.5, and so on. This is to minimize reabsorption of emitted photons by the sample.

3. Once a sufficiently dilute solution has been prepared, take an absorption spectrum of the solution, making sure to obtain the absorption peak in the spectrum. Take an absorption spectrum in the same range of just the solvent used so that it may be subtracted off from the sample's spectrum. Find the max absorbance at the peak and record this number.
4. Take an emission spectrum of the sample at this absorbance using the wavelength of maximum absorption for excitation, making sure to take lamp spectrum into account. Make sure that the spectrum taken includes the emission peak.
5. Prepare a sample of a different absorbance/concentration than previously used and repeat the above process (steps 3-4). This is easily done if the solution is near the max absorbance for the given cuvette, as one can simply dilute the sample and proceed with the measurement.
6. It is imperative that the wavelength range of the emission spectrum in step 4, as well as the slit widths and integration time, be kept constant for every measurement. If any of these parameters are varied, it can contaminate the results of the quantum yield measurement.
7. Once a sufficient number of absorbances and emission spectra have been measured, numerically integrate each emission spectrum to find the integrated fluorescence intensity. Plot the integrates fluorescence intensity as a function of absorbance. The result of this should be a straight line.
8. If the relationship is sufficiently linear, use Eq. 6 to find the quantum yield of your sample. For best results, two quantum yield standards should be used as the knowns in Eq. 6. Perform the calculations using one of the standards and your sample of unknown QY, then use the data for the other standard and your sample. Then average the two QY values you obtain.

Appendix B

An alternative to the lengthy QY measurement detailed in this paper is through Eq. 7:

$$\Phi_U = \Phi_K \left(\frac{S_{U,max}}{S_{K,max}} \right) \quad (7)$$

where $S_{U,max}$ and $S_{K,max}$ are the peak values from the emission curves of the sample of unknown QY and the QY standard, respectively. All that needs be done is to take an emission spectrum (making sure to adjust for lamp intensity) that includes the emission peak of the compound. Measuring the standards is unnecessary, as Figure A1 includes two curves (and their corresponding equations) that can be used to determine the corresponding peak value to be used for $S_{K,max}$. The ratio of the two peak values multiplied with the corresponding QY value of the standard whose curve is used is sufficient to get a rough estimate of QY.

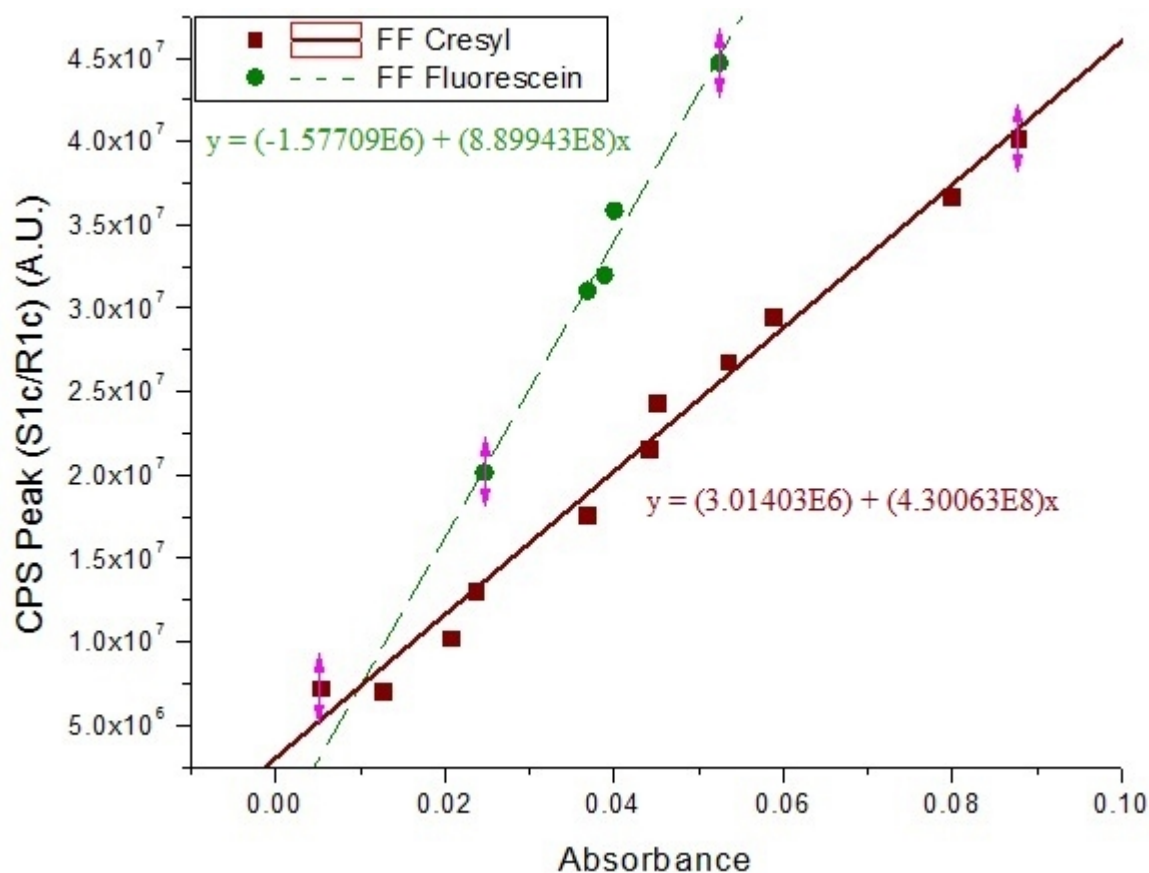


Figure A1 – The information in this plot can be used to determine QY values quickly and simply.

The best results for this quick measurement are for absorbances between 0.02 and 0.05.

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