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# Instrument Building for Detection of Triplet Signal from Quinolinone Molecules

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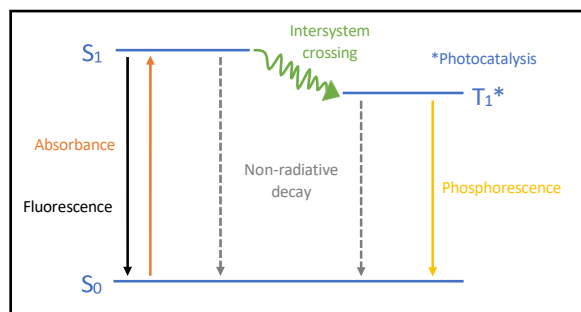
**ABSTRACT** Conjugated organic molecules such as the 2-quinolinone family can be used as energy-donor molecules in photocatalysis because of their light absorbing and energy transmitting qualities. Good donor molecules have triplet excited states that are useful for photocatalysis due to their long lifetimes. The goal of this research was to build a near-infrared spectroscopy instrument to observe a triplet emission signal in a set of five previously synthesized 2-quinolinone molecules. A near-infrared absorbance instrument was built successfully with accurate measurements; however, there was no detection of the desired triplet emission signal.

## INTRODUCTION

Photocatalysis can drive reactions by converting light energy into chemical energy using light-absorbing molecules, photocatalysts. The photocatalysts then transfer the energy to the molecules participating in the reaction, driving reactions that may not otherwise occur. In order to obtain a photocatalyst molecule, it first needs to be excited through a strong light source. This is where a molecule absorbs light, called absorbance (Figure 1, orange arrow). In the figure, the molecule starts as a ground singlet state,  $S_0$ , then upon absorption of light, the molecule achieves its first excited state,  $S_1$ , containing two paired, opposite spin electrons. Then through spontaneous conversion of the electron spins becoming unpaired and changing to same the spin, it is converted to a triplet excited state,  $T_1$ , called intersystem crossing (Figure 1, green arrow).

The use of this excited triplet state can now act as a photocatalyst and is useful for photocatalysis, as a donor molecule, to push a reaction forward that might not otherwise occur. The formation of a triplet state, however, is forbidden, meaning that this reaction is less probable due to the altered spin electrons. Thus, measuring this signal is challenging due to its weak absorbance, decreased probability and competes with

fluorescence and non-radiative decay (Figure 1). Phosphorescence is also a forbidden process as it is the emission of an excited triplet state to its ground singlet state and occurs much slower than that of an allowed transition state,  $10^4$  seconds slower (Figure 1, yellow arrow). Thus, this triplet



**Figure 1.** Jablonski diagram characterizing singlet and triplet states for use in photocatalysis.

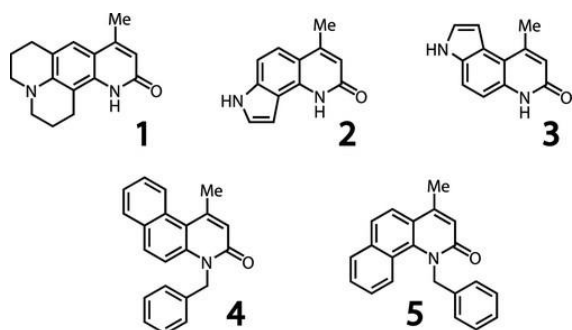
state is more desirable due to its same spin electrons inducing a slower decaying rate and more stable, longer lifetime. This makes triplet excited states particularly useful in photocatalysis giving them a long time to transfer the absorbed energy into the reacting molecules.

Photocatalysts, specifically Quinolinones, have been previously studied to be potential drugs for

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cancer treatments.<sup>1,2</sup> They have been explored for being a dye molecule in fluorescence resonance energy transfer (FRET) and other optical applications.<sup>1</sup> From the five 2-quinolinone molecules that were previously studied by Prof. Vadola and Dr. Griffin,<sup>1</sup> it was found that compounds **4** and **5** have the strongest transient absorption data as well as having longer relative triplet populations compared to the other three compounds (Figure 2). Compounds **4** and **5** have an additional fused benzene ring to the 2-quinolinone core. Quinolinone molecules were compared to the previously studied coumarins



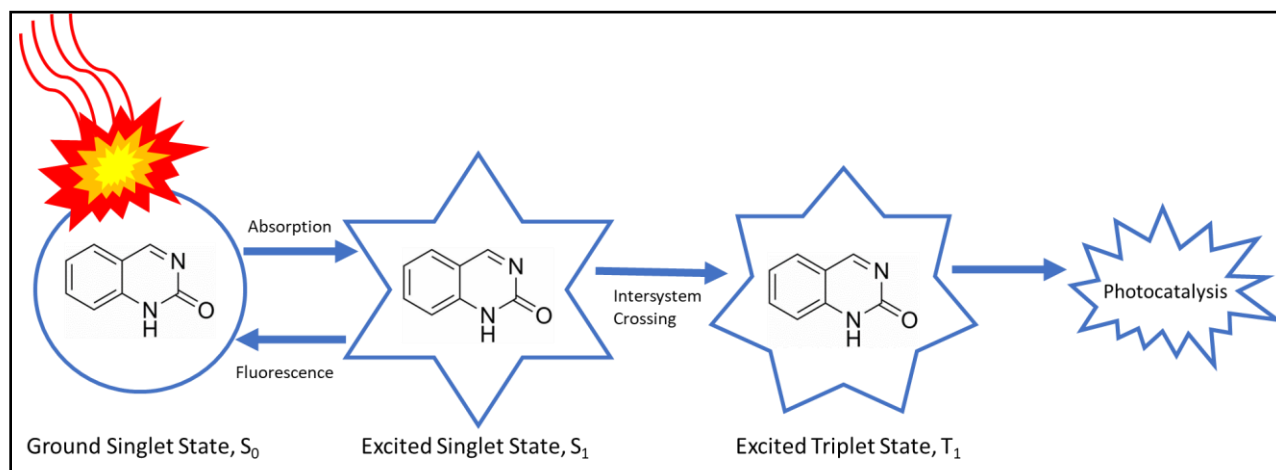
**Figure 2.** 2-Quinolinone family as presented in Professor Vadola's and Dr. Griffin's previous experiment.<sup>1</sup>

which are similar in structure, where coumarins contain an oxygen atom rather than a nitrogen atom in the lactam group. It was found that quinolinone molecules had an increase in triplet yield due to excitation compared to the

coumarins.<sup>1</sup> Therefore the 2-quinolinone structure is preferred as an absorbing donor molecule, useful for photocatalysis, and more effective for this experiment. Figure 3 illustrates the process in which the parent compound of the 2-quinolinone family undergoes to achieve photocatalysis. While it was concluded that compounds **4** and **5** had longer relative triplet populations, it is still uncertain the mechanism of the triplet formation. Further experimentation is needed to fully characterize the triplet spectroscopy and to obtain a less ambiguous signal.

Thus, our study asked how excited triplet signals in Quinolinone molecules can be detected and differentiated from singlet signals. The goal of this study is to directly observe the triplet signals to determine if the 2-quinolinones of interest contain a strong energy signal as well as being environmentally conservative by using photocatalysis, a safe, radiative technique to catalyze reactions.

To detect the emission of the desired triplet signals, an emissions instrument had to be built due to DePaul's laboratories not having an effective spectrometer to measure in the near-infrared range, the range in which the triplet signals emit. A spectrometer is an instrument used to measure the photons of light and convert them into readable spectra and absorbance or fluorescence data. To build one, a strong light source and a sensitive photodetector are needed.

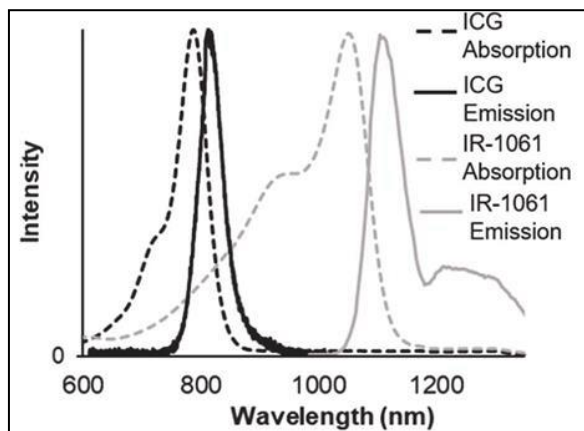


**Figure 3.** Summary of the parent 2-quinolinone compound being made useful for photocatalysis through the illustration of the ground singlet state being excited by a light source, then through intersystem crossing to the excited triplet state, which is useful in photocatalysis.

Thus, different light sources and detectors were explored along with different dyes to mimic the desired spectrum of the triplet signal.

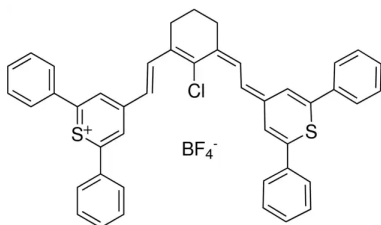
## METHODS

The dyes IR-1061 and Oxazine 170 perchlorate were used to mimic certain absorption and emission signals that were of interest. Firstly, the dye, IR-1061 (Sigma-Aldrich 80%, 749.13 g/mol) is known to absorb at 1061 nm. This dye was used to mimic a singlet oxygen emission signal, 1280 nm, to test if the instrument can read the correct signal. Determination of a correct spectrum was compared to previous research on the dye as shown by the grey dotted and solid lines (Figure 4).



**Figure 4.** Known absorbance of Indocyanine Green (ICG) at 814 nm and IR-1061 dye at 1061 nm.<sup>6</sup>

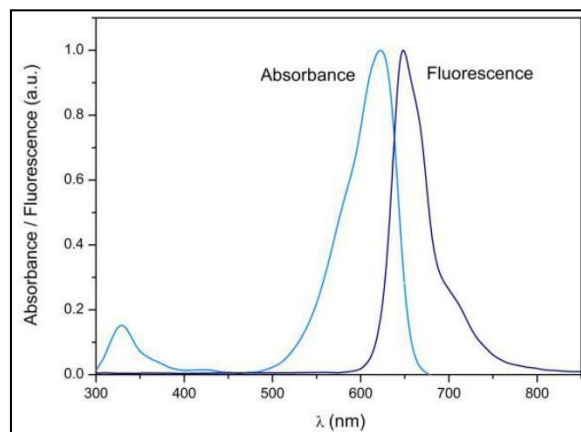
The chemical compound of IR-1061 dye used in the experiment is illustrated (Figure 5).



**Figure 5.** Chemical structure of IR-1061 (Sigma-Aldrich 80%, 749.13 g/mol) dye.

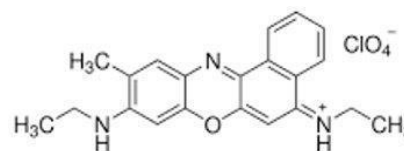
The second dye tested was Oxazine 170 perchlorate (Sigma Aldrich 95%, 431.87 g/mol).

It is known to absorb at 613 nm, mimicking the signal of a well-studied photocatalyst  $\text{Ru}(\text{bpy})_3\text{Cl}_2$ . In the study, the goal was to use  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  as it is known to successfully emit a triplet signal.<sup>3,4</sup> However, there was no success in retrieving a signal for  $\text{Ru}(\text{bpy})_3\text{Cl}_2$ . To determine a correct spectrum of Oxazine 170 perchlorate, its spectrum was compared to previous literature (Figure 6).



**Figure 6.** Known absorbance and fluorescence of Oxazine 170 perchlorate at 613 nm.<sup>5</sup>

The chemical compound of Oxazine 170 perchlorate used in the experiment is illustrated (Figure 7).



**Figure 7.** Chemical structure of Oxazine 170 perchlorate (Sigma Aldrich 95%, 431.87 g/mol) dye.

To build the instrument, an optical table with a strong light source, various lenses and irises, and an oscillator were used to direct a beam of light through the sample and into the spectrometer and photodetector. Thus, the beam of light from the light source was collimated through the lenses and irises into the spectrometer and photodetector to achieve the most intense light signal. Utilization of an oscilloscope was used to measure and monitor the light signal to the face of photodetector. The higher the amplitude of the



sigmodal wave on the oscillator correlated to the columnated light being shown directly on the face of the photodetector. When the amplitude was optimized, the signal from the photodetector was then transferred to a Lock-In Amplifier, which can extract the desired light signals from a noisy background. The Lock-In Amplifier is a very sensitive instrument and can measure light signals all the way down to nanovolts. The settings of the amplifier were optimized to obtain a clean spectrum without background noise. The data extracted from the Lock-In Amplifier and spectrum created were read from a computer software program, SynerJy, and created in Excel.

The specific light source used was the SLS202L(M) Stabilized Tungsten light source from Thor Labs (Figure 8). The goal was to columnize the beam of light shown in Figure 8 by the yellow blocks and triangles. Through each lens and iris, it diffracts and focuses until it reaches the spectrometer (Figure 8-A). First, it starts with a 25 mm biconvex lens that focuses the incident light from the light source (Figure 8-1). Then, an iris is used to start the columniation process by only allowing for the most focused beam of light through (Figure 8-2). An oscillator is then used to create pulses of desired frequency

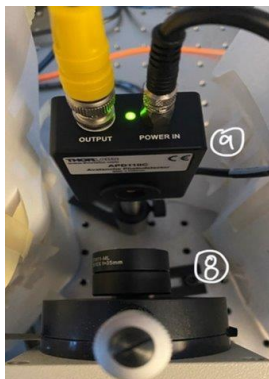
from a continuous source of light for the photodetector to read it into electrical signals for absorbance spectrum calculations (Figure 8-3). Next, a 50 mm biconvex lens was used to further focus the beam of light (Figure 8-4) along with an iris to block out the refracted light (Figure 8-5). A cuvette holder was placed in the beam of light to measure the desired dyes and compounds (Figure 8-6). Lastly, a 35 mm plano-convex lens was utilized to further focus and intensify the light signal (Figure 8-7) onto the opening of the Horiba Scientific MicroHR spectrometer (Figure 8-A). The spectrometer has two gradients, 1200 and 600 grooves/mm corresponding to a 500 and 1000 nm Blaze respectively. Once the columnized beam enters the MicroHR spectrometer it will reflect to the other opening through another lens and finally to the Avalanche photodetector APD 110C (Figure 8-8, 8-9). Paper scraps were used to minimize the background light to obtain the most accurate measurement.

Close up images of the instrument are included, where the beam of light is columnated into the MicroHR and then fractured out the other opening on to the photodetector (Figure 9). The optimization of this instrument was crucial to



**Figure 8.** Side view of instrument. The red column is the tungsten light source, 25 mm biconvex lens (1), iris (2), oscillator (3), 50 mm biconvex lens (4), iris (5), cuvette holder (6), and 35 mm plano-convex lens (7). The SLS202L(M), Stabilized Tungsten light sources was used from Thor Labs. The settings on Lock-In Amplifier used were 2 x 1 mV.

determine the most accurate spectrum of the dye molecules and desired compounds.



**Figure 9.** Top view of 8 and 9: 35 mm biconvex lens (8), Avalanche Photodiode APD 110C (9) (900-1100nm).

The optimized instrument was then used to measure spectra of the desired molecules and dye compounds.

## RESULTS AND DISCUSSION

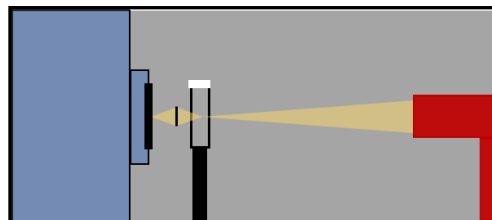
The determination of the triplet signal was not successful in either the 2-quinolinone compounds or  $\text{Ru}(\text{bpy})_3\text{Cl}_2$ . The results consisted of successfully obtaining two strong spectra, Oxazine 170 perchlorate and IR-1061 dye. To calculate an absorbance spectrum from the instrument, the absorbance equation was used (Equation 1).

$$A = -\log (\%T) \quad (1)$$

In Equation 1, A is absorbance and T is transmittance, the fraction of incident light transmitted through the substance. More specifically the transmittance value is where the incident light, or light without any solution in the cuvette holder is measured first, . Then, when the solution is in the cuvette holder, another measurement is taken, called sample spectra (Equation 2).

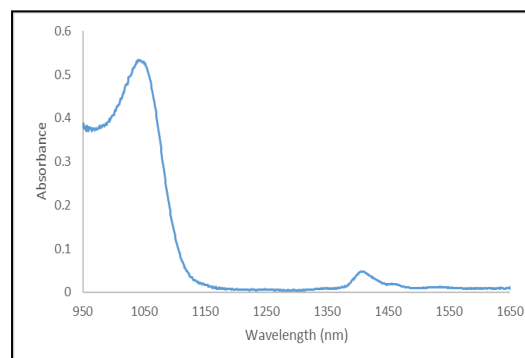
$$\%T = \frac{\text{incident spectra}}{\text{sample spectra}} \quad (2)$$

These two values are then subtracted from each other and multiplied by 100 to obtain a percentage of T and then the negative log of %T is taken using Equation 1. The absorbance is then graphed versus the wavelengths correlated to those values. An illustration is included to explain these measurements in simpler illustrations from the instrument built (Figure 10). The first measurement is the incident or natural beam of



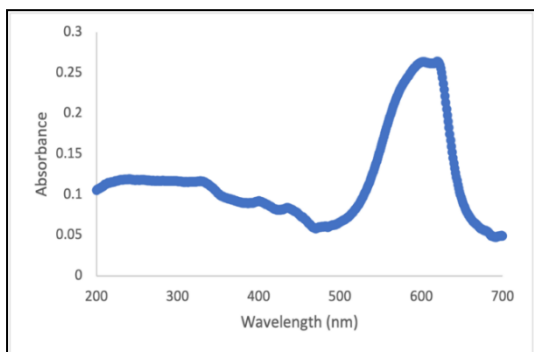
**Figure 10.** Illustration of how the measurements were taken without lenses, iris and oscillator.

light, denoted as the yellow triangles projected from the red tungsten light source is taken without the sample (empty cuvette) and into the blue spectrometer. The second measurement is when the sample is in the beam of light (a full cuvette). The full cuvette reading is then subtracted from the empty cuvette and multiplied by 100 to obtain the fraction of incident light, %T. Thus, calculating absorbance for the sample in the instrument was performed. From these calculations the dye spectrum of IR-1061 was successfully obtained yielding an absorbance peak of 0.5327 at 1044 nm (Figure 11). The spectrum was compared to its literature values, previously illustrated (refer to Figure 4).



**Figure 11.** IR-1061 dye in acetonitrile spectrum taken on instrument at 1044 nm.

The spectrum of the dye Oxazine 170 perchlorate was also successfully measured, where it obtained an absorbance peak of 0.2641 at 620 nm (Figure 12). It correctly correlated to its previous research values (refer to Figure 5).



**Figure 12.** Absorbance of Oxazine 170 perchlorate 0.0006 g of in 250 mL in acetonitrile at 620 nm.

The triplet signal spectra of the desired 2-quinolinone compounds **4** and **5** or the spectra of  $\text{Ru}(\text{bpy})_3\text{Cl}_2$ , were not obtained. However, successful measurement of two dyes were collected. With the triplet signal being a

forbidden signal, it was challenging to obtain. Other techniques such as, deoxygenation of the solution, will eliminate oxygen in the solution, creating less molecules for the triplet state to interact with. Thus, yielding a stronger emissions spectrum. Another technique that can be used is that of a high-powered UV LED light source in hopes to detect the weak triplet signal, from the 2-quinolinone molecules of interest.

## CONCLUSION

Photocatalysis is a useful process in order to obtain triplet states in molecules. In search of these signals, a near-infrared emission spectroscopy instrument had to be built. The measurement of the triplet states in the quinolinone molecules have not yet been observed. Rather an absorbance spectroscopy instrument was successfully built obtaining replicable spectra of previously studied dyes, IR-1061 and Oxazine 170 perchlorate. The observation of triplet states is still being researched by implementing new techniques such as deoxygenating the solution to indirectly observe the triple signal, as well as use of a much stronger light source.

## ACKNOWLEDGMENTS

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## REFERENCES

- (1) Fligelman, Alana, et al. Electronic Relaxation Dynamics in 2-Quinolinones with Extended Conjugation. *The Journal of Physical Chemistry* [Online] **2021**, vol. 125, no. 45, pp. 9757–9769. <https://doi.org/10.1021/acs.jpca.1c04560>
- (2) Crous, A., Abrahamse, H. Targeted Photodynamic Therapy for Improved Lung Cancer Treatment. In (Ed.), *Lung Cancer - Strategies for Diagnosis and Treatment. IntechOpen.* [Online] **2018**. <https://doi.org/10.5772/intechopen.78699>
- (3) Pitre, S., McTiernan, C., Vine, W. *et al.* Visible-Light Actinometry and Intermittent Illumination as Convenient Tools to Study  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  Mediated Photoredox Transformations. *Sci Rep* **5**, 16397 [Online] **2015**. <https://doi.org/10.1038/srep16397>
- (4) Zhang, H.; Jin, Q.; Song, X.; Li, H.; Jia, D.; Liu, T. Oxazine-Functionalized CdSe/Zns Quantum Dots for Photochemical Ph Sensing. *ACS Applied Nano Materials* [Online] **2020**, *3* (11), 10996–11006. <https://pubs.acs.org/doi/pdf/10.1021/acsnm.0c02219>



- (5) Miluski, P. Luminescent Properties of Oxazine 170 Perchlorate Doped PMMA Fiber. *Fibers* [Online] **2017**, 5, 15. <https://doi.org/10.3390/fib5020015>
- (6) Yeroslavsky, G., Umezawa, M., Okubo, K., Nigoghossian, K. Photostabilization of Indocyanine Green Dye by Energy Transfer in Phospholipid-PEG Micelles. *Journal of Photopolymer Science and Technology* [Online] **2019**. 32. 115–121. 10.2494/photopolymer.32.115.