Modeling Sensitizer to Annihilator Ratios for Optimal Light Intensity in Triplet-Triplet Annihilation Upconversion

Grant Proposal

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Abstract

Triplet-triplet annihilation upconversion (TTA-UC) is the organic chemical process of upconverting low-energy light to high-energy light. This is done through the TTA-UC system, including the sensitizer, annihilator, and the solvent. The ratio of the sensitizer to the annihilator affects the efficiency of the system and primarily the intensity of the light produced. The optimal ratios for TTA-UC pairings are commonly known, but their effect on light intensity has not been well modeled. The goal of this experiment was to test a variety of ratios for a sensitizer-annihilator pairing and model it on a graph, created to predict the light intensity from a given ratio. 6 different ratios of a TTA-UC system were observed using a spectrofluorometer to find how light intensity changes with an increasing amount of annihilator. It was found that doubling the amount of annihilator from 1:50 to 1:100 created 2.47 times increase on peak light intensity. However, increasing the concentration to 1:200 resulted in no light intensity being produced. It's clear that light intensity and concentration do not have a liner relationship, but rather one that increases rapidly at first, then quickly drops due to inefficiency in the system. Understanding how specific ratios affect light intensity is important because researchers do not always desire the brightest output. In biological applications, TTA-UC can be used for deep tissue imaging. However, if the upconverted light is too intense, it can cause damage to cells. Next steps include refining the model and expanding it to apply to different TTA-UC pairings.

Keywords: *TTA-UC, sensitizer, annihilator, upconversion, wavelength, photon*

Modeling Sensitizer to Annihilator Ratios for Optimal Light Intensity in TTA Upconversion

Triplet-triplet annihilation upconversion (TTA-UC) is the process of converting two low-energy photons into a single high-energy photon. In effect, this converts low energy light, such as red light, to high energy light, such as blue or UV light. It was first theorized in the 1960s, but its practical application only gained traction in the 2000s (Naimovičius et al., 2023). Today, there are a variety of studies on TTA-UC and how its process can be applied in 3D printing, solar panels, and even drug delivery (Naimovičius et al., 2023).

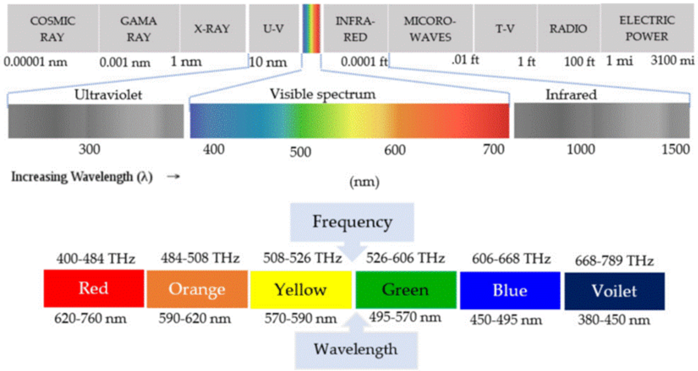

Figure 1
Diagram of the Light Spectrum
(Chou et al., 2021)

Sensitizer

A sensitizer is a molecule that absorbs low energy, which is usually around 650 nm or wavelength of the red light (Chou et al., 2021). This can be seen in Figure 1 on the right side of the visible spectrum. When the sensitizer absorbs the energy from the photon, it is promoted to its first excited singlet state (S_1). S_1 describes the state of the sensitizer molecule's electron when it has been elevated to a higher-energy orbital. The molecule then undergoes a process called intersystem crossing (ISC). Here, the electron changes its spin and the molecule changes from S_1 to a triplet excited state (T_1). The stored excitation in T_1 is transferred to the annihilator through triplet-triplet energy transfer, shortened as TTET (Feng et al., 2025).

Annihilator

The annihilator is a molecule that receives energy from the sensitizer and produce higher-energy photons. It receives energy from the sensitizer through TTET, a process where two molecules' electron orbitals overlap and can exchange energy directly without emitting light. The transfer produces an excited state called triplet exciton on the annihilator. When two triplet-excited annihilator molecules encounter each other, they undergo triplet-triplet annihilation (TTA). Here, two triplet excited molecules combine to produce one higher-energy singlet excited state on one annihilator molecule. Essentially, the energy from two excitons is put onto only one of them, increasing one's energy while reducing the others. The singlet state molecule returns to its ground state, releasing a photon of higher energy which has a shorter wavelength (Feng et al., 2025). In Figure 1, the emitted light will be anywhere on the left side of the light spectrum.

Sensitizer and Annihilator Pairings

Every type of sensitizer and annihilator is unique, meaning they each absorb and emit different wavelengths of light. For example, the sensitizer PdTPBP absorbs 630-650 nm (red light) while the sensitizer PtOEP absorbs 540-580 nm (green light) (Huang et al., 2021). Every sensitizer has an absorption spectrum, describing the energy levels they can absorb, however, wavelengths at the ends of the spectrum won't be absorbed as efficiently as wavelengths in the middle (peak absorption). On the other hand, annihilators have an emission spectrum, the wavelength of light they produce. The annihilator rubrene emits 560-580 nm, while perylene emits 460-480 nm (Chakkamalayath & Kamat, 2023). It is essential to choose a sensitizer and annihilator pair that will work together to ensure TTET can occur. To ensure the pairing will work, the sensitizer energy of T_1 must be slightly higher than the annihilator energy of T_1. This is so that the energy can flow downhill during TTET. The difference of 0.05-0.02 eV between sensitizer and annihilator is optimal. Different pairings of sensitizers and annihilators have been well-researched, common ones including PdTPBP and perylene, as well as PdOEP and rubrene (Baronas et al., 2025).

TTA-UC Systems

TTA-UC systems refer to the complete system used for upconversion in an experiment. This will include the sensitizer, annihilator, and typically, a solvent. The solvent allows the sensitizer and annihilator to be diluted and interact with each other. Common solvents for TTA-UC include tetrahydrofuran (THF) and Toluene (Wei et al., 2020).

Oxygen Quenching

Oxygen quenching is a large problem faced in TTA-UC systems. Triplet states of the sensitizer and annihilator are very sensitive to collisions with oxygen, since O_2 in its ground state is a triplet. Therefore, the triplet states of the sensitizer and annihilator can collide with O_2, which consumes energy and is not the goal. A workaround is degassing the TTA-UC system by replacing the oxygen in the test tube with another gas that does not quench triplet states, including nitrogen and argon (Wan et al., 2023).

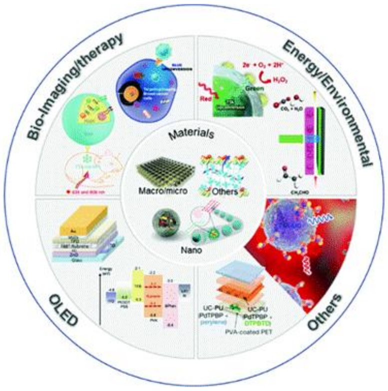

Figure 2
Graphic of Different Applications of TTA-UC
(Seo et al., 2022)

Applications

Research on TTA-UC has led to its utility in many different fields as seen in Figure 2. Primarily, TTA-UC enables curing of opaque and thick hydrogels. This is because the longer wavelengths, red light, can penetrate deeper into the hydrogel, through opaque or thick layers. Then, the TTA-UC system upconverts the red light to UV light which cures the hydrogel into a solid. Therefore, TTA-UC is applicable in 3D printing hydrogels and curing them into a solid, otherwise known as photopolymerization (Seo et al., 2022).

Additionally, TTA-UC systems can be used to convert red and near infrared sunlight into higher energy photons for better absorption in solar panels. This could increase solar panel efficiency by 10% (Seo et al., 2022).

TTA-UC systems also have use in medicine. It can be used for bioimaging and drug delivery due to red light being able to penetrate through tissues (Seo et al., 2022). However, if the higher-energy light produced is too intense, it can stress and damage cells. Sometimes, it is desirable to have lower efficiency in the TTA-UC system to ensure the correct light intensity is produced. Due to this, understanding how the ratio between sensitizers and annihilators affect light intensity is crucial.

Section II: Specific Aims

This proposal's objective is to model how the ratio between the sensitizer and annihilator affects the intensity of light produced for a variety of sensitizer-annihilator pairings.

The long-term goal is to create a database that can help researchers find what ratios to use in their experiment for their desired final light intensity. The central hypothesis of this proposal is that the light intensity will rise as the ratio increases before hitting a peak and then dropping off. The rationale is that an optimal ratio for pairings is known, and that going over or under it will decrease the light intensity (Durandin et al., 2019). However, quantifying the decrease has not been well studied. Researchers would benefit from knowing how a change in the optimal ratio affects final light intensity. The work proposed here will benefit future research in TTA-UC by providing understanding of the relationship between sensitizer, annihilator, and light intensity.

Specific Aim 1: Test 6 different ratios for each pairing and observe light intensity

Specific Aim 2: Model the data collected on a graph and find trends/formula

The expected outcome of this work is a general trend or formula that researchers can refer to when looking for a specific ratio to use for their pairing.

Section III: Project Goals and Methodology

Relevance/Significance

Collecting data and modeling how the ratio between sensitizer and annihilators affect light intensity will help future researchers design their TTA-UC systems more effectively. In biomedical applications, light that is too intense can stress and kill cells (Kim et al., 2023). This makes TTA-UC systems unsuitable to use as in biological environments. However, if a lower intensity of light can be produced by utilizing a lower ratio, then this method can be applied. Furthermore, higher ratios typically will require more microliters of sensitizers and annihilators for researchers to use. However, since these chemicals are typically expensive, the data from this project can help researchers choose a ratio that compromises on their desired light intensity and how much material they want to use per sample. Overall, better understanding these ratios' effect on light intensity by modeling them will help future research on TTA-UC systems.

Innovation

Previous research has been conducted to identify the optimal ratios, which are the ratios that produce the highest light intensity, for various sensitizer and annihilator pairs. However, this project will be exploring and collecting data on the ranges that are more commonly ignored: lower light intensities. Furthermore, a mathematical trend will be designed to describe the relationship between the ratio and light intensity, aiding researchers in better understanding and choosing a ratio for their project.

Methodology

Creating the TTA-UC Sample

1. Micropipette 2 μL of tetrahydrofuran (THF) into a standard cuvette.
2. Micropipette the appropriate amount of μL of sensitizer into the cuvette to create the ratio.
3. Micropipette the appropriate amount of μL of annihilator into the cuvette to create the ratio.
4. Put on a rubber stopper onto the cuvette and lightly shake to mix the chemicals
5. Inside the fume hood, insert the exit needle (where air will exit through)
6. Insert the long needle connected to the source of argon so it reaches the bottom of the cuvette
7. Wait 5 minutes
8. Remove the needles once bubbles have stopped appearing (air has been replaced with argon)
9. Take off the rubber stopper and screw on the plastic lid

Testing the TTA-UC Sample

1. In the dark room, shine a red laser of 650 nanometers
2. Set up the spectrofluorometer and turn it on
3. Place the cuvette inside and close the lid
4. On the computer, select a range of 400 to 550 nanometers and data collection at every 1 nm.
5. Observe the data output and properly save it

Specific Aim #1: Test 6 different ratios for each pairing and observe light intensity

The objective is to graph a variety of ratios between sensitizers to annihilators. The approach is to test 1:0 (as a control), 1:50, 1:100, 1:150, 1:175, and 1:200 ratios for the pairing of sensitizer and annihilator. To do this, the TTA-UC system will be created in cuvettes using THF as a solvent, and the appropriate concentrations of sensitizer to annihilator for each ratio. The data collected will be the light intensity produced for each sample as collected by a spectrofluorometer, which is an instrument that measures light intensity of a sample after exciting it from a given range of light. Our rationale for this approach is that by testing various ratios, data can be collected and observed to see whether a trend exists between increasing ratios and peak light intensity. Additionally, data can be collected to find how the variety of initial wavelengths of light used to excite the sample affects the light intensity produced as well.

Justification and Feasibility.

The process for specific aim #1 includes creating a TTA-UC system in THF and testing it using a spectrofluorometer. This process is widely used in the field in prepping and testing their TTA-UC systems before incorporating them into applications. For example, TTA-UC systems were created in various solvents and tested using a spectrofluorometer in a paper from 2021 (Huang et al., 2021). The diagram below from a paper in 2023 displays the process of how a spectrofluorometer collects data (Park et al., 2023). Wavelengths of light increasing by 1 nanometer from 400 to 550 nm are shone on the sample. The light intensity produced for each is recorded by the instrument. This allows for a quick and accurate analysis to find the light intensities possible depending on the wavelength of the excitation light.

Summary of Preliminary Data

To start, I decided to model 2 of the most common ratios, 1:50 and 1:100, for perylene and PdTPBP. These produced a light intensity of 3,000,000 CPS and 15,700,000 CPS respectively. There is a 423.3% increase in light intensity from the first to the second sample, meaning the ratio undeniably affects light intensity. While the shapes of both graphs look similar, the scale of the y-axes on both differ greatly. The intensity in figure 1 and figure 2 below also support how much brighter the 1:100 sample is compared to the 1:50.

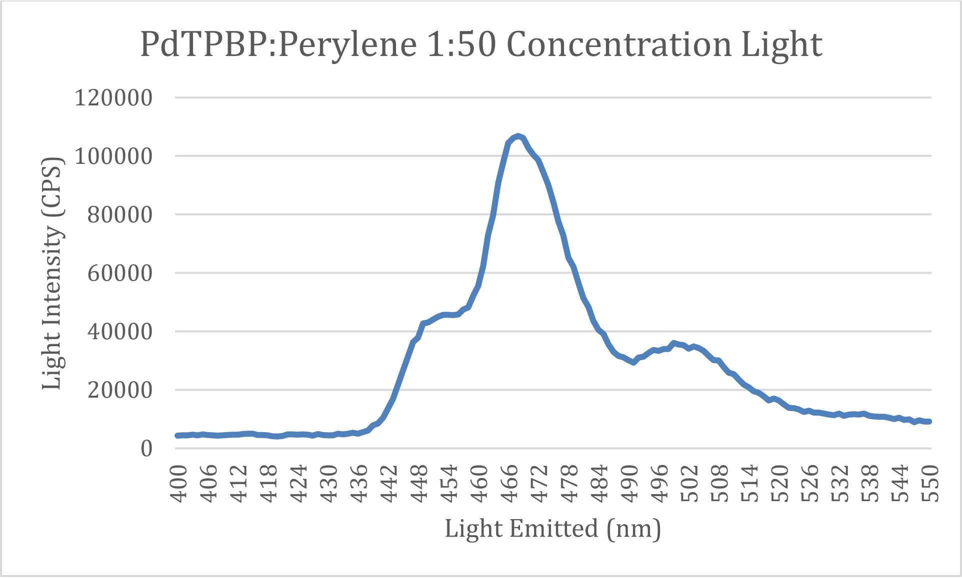

Figure 1: 1:50 Ratio of PdTPBP to Perylene and Light Intensity

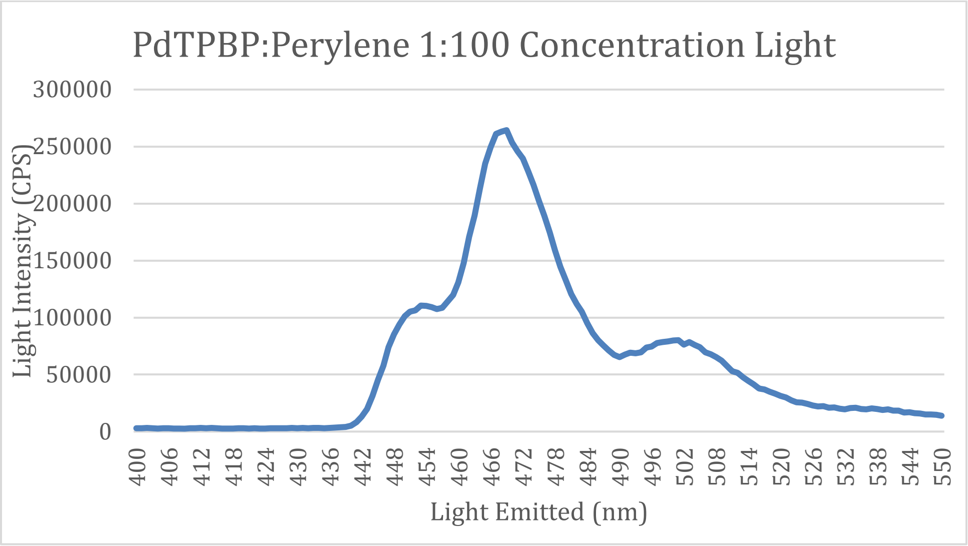

Figure 2: 1:100 Ratio of PdTPBP to Perylene and Light Intensity

Expected Outcomes

The overall outcome of this aim is to collect data on how ratios affect light intensity. The more data collected initially will lead to a better overall understanding in the end. The pairing, ratio, and corresponding graphs of light intensity will all be tracked. This knowledge will be used for the next specific aim, creating a mathematical trend to identify the ratio needed for a desired light intensity.

Potential Pitfalls and Alternative Strategies

We expect that there may be some issues arising in the degassing portion of the process. Using the needles can be dangerous and therefore will be handled only inside the fume hood. Additionally, some other problems that may arise are the fact that the spectrofluorometer will stop running if faced with light that is too intense. This is because the light may damage the instrument, so it stops running before it reaches the damaging point. In this case, data will have to be noted down as the light intensity was about the damaging point. Light of this high intensity is likely not desirable to researchers due to its ability to harm optical instruments.

Specific Aim #2: Model the data collected on a graph and find trends/formula

The objective is to graph the data collected from specific aim #1. The x-axis will be the ratios between annihilator to sensitizer which will always be greater than 1 as annihilators are typically 50 times the concentration of a sensitizer in a sample. The y-axis will have the peak light intensity for each ratio. The graphing software, Desmos, will be utilized. By analyzing the graph, a mathematical trend will be created to describe the relationship between the ratio and light intensity for a given pairing. The rationale for this approach is that graphing data and performing a regression analysis to find a proper relationship of best fit is commonly used.

Justification and Feasibility.

The process for specific aim #2 includes graphing the data collected and analyzing it to design a mathematical model. This process is widely used by students, teachers, and researchers in every field. Specifically, I hypothesize that the relationship will look like an asymmetrical bell curve with a left skew. It is known that it takes some time for the light intensity to increase when at low ratios. Then it jumps up rapidly closer to the peak and drops off faster than it rose.

Expected Outcomes

The overall outcome of this aim is to design a mathematical model that describes the relationship between the ratio and light intensity from the data collected. The more data collected initially will lead to a more accurate model. The type of relationship the data most closely fits can give clues into how they function and what they may behave similarly to. This model will be used for the next specific aim, testing new ratios to confirm whether the model is accurate.

Potential Pitfalls and Alternative Strategies

We expect that there may be some problems in designing a model that fits closely enough with the data collected. The goal is to find a model that fits the data with a R^2 of 0.95. If this is not accomplished, the best model can be used to analyze the relationship. Furthermore, the reasons as to why the data does not fit a model well can be analyzed. It could be due to human inaccuracies during testing or a quality of the TTA-UC system.

Section IV: Resources/Equipment

The resources and equipment used will be provided by the Han Lab in the Lazare Medical Research Building at UMass Chan Medical School. The projected materials used will be the pairing of sensitizer and annihilator, PdTPBP and perylene. The solvent THF will be used to dilute the mixtures. Argon will be used to degas the samples so that oxygen quenching does not occur. Tools to conduct the experiment will include cuvettes, which are a rectangular transparent tube used to hold liquid samples for optical analysis. Additionally, micropipettes and pipette tips will be used. Rubber stoppers and needles will be used for the purpose of degassing the samples. Acetone will be used to clean and wash the cuvettes after use. The instruments to observe optical qualities of the samples will be a red-light lamp and a spectrofluorometer. The spectrofluorometer will provide measurements of light intensity produced after the sample is excited by a specific wavelength. For the modeling part of this project, online software including Excel and Desmos will be utilized. Lastly, to confirm the accuracy of the model created, all the tools listed above will be used to test a variety of ratios to see if the light produced was predicted correctly by the graph.

Section V: Ethical Considerations

Some ethical considerations are that the chemicals used can be dangerous if handled improperly. Therefore, proper personal protective equipment will be worn at all times. This includes a lab coat, eye goggles, and gloves. Additionally, the hazardous chemicals must always be disposed of in the correct disposal and washed out with acetone. This is to ensure that the chemicals do not reach the environment or contaminate the regular water pipes. Lastly, red light and lasers will be used on the samples to observe their reactions. Lasers can be very dangerous for a human's eyes, so it will be ensured that no one looks at the laser directly. Additionally, no reflective jewelry will be worn.

Section VI: Timeline

Dec 8-Dec 20: Collect initial ratios 0:1, 1:50, 1:100 and record light intensity measurements using spectrofluorometer (2 trials each)

Dec 21-Jan 5: Collect additional ratios in ranges where intensity shows big jumps (1:150, 1:175, 1:200)

Jan 6-Jan 12: Average data, check for outliers, prepare dataset for plotting

Jan 13-Jan 17: Graph ratio vs. light intensity (full dataset) and inspect trends

Jan 18-Jan 22: Fit a mathematical trend (choose between candidate models) and pick the best-fit by error metrics (R^2>0.95)

Jan 23-Jan 26: Use the model to predict light intensities for untested ratios and select 3–5 target ratios to validate

Jan 27-Jan 30: Run validation experiments on chosen ratios and compare observed intensities to model predictions

Section VIII: References

Baronas, P., Lekavičius, J., Majdecki, M., Elholm, J. L., Kazlauskas, K., Gaweł, P., & Moth-Poulsen, K. (2025). Automated Research Platform for development of triplet–triplet annihilation photon upconversion systems. *ACS Central Science*, *11*(3), 413–421. https://doi.org/10.1021/acscentsci.4c02059

Chakkamalayath, J., & Kamat, P. V. (2023). Directing singlet excited energy flow in rubrene-perylene dye (DBP) films. *The Journal of Physical Chemistry C*, *127*(33), 16312–16318. https://doi.org/10.1021/acs.jpcc.3c04003

Chou, C.-F., Tsai, C.-M., Chen, C.-H., Wong, Y.-H., Fang, Y.-C., Wen, C.-C., Lee, H.-Y., Le, H.-T., Chang, S.-H., & Liao, H.-Y. (2021). Optical design and optimization with genetic algorithm for high-resolution optics applied to underwater remote-sensing. *Applied Sciences*, *11*(21), 10200. https://doi.org/10.3390/app112110200

Durandin, N. A., Isokuortti, J., Efimov, A., Vuorimaa-Laukkanen, E., Tkachenko, N. V., & Laaksonen, T. (2019). Critical sensitizer quality attributes for efficient triplet–triplet annihilation upconversion with low power density thresholds. *The Journal of Physical Chemistry C*, *123*(37), 22865–22872. https://doi.org/10.1021/acs.jpcc.9b08026

Feng, H.-J., Zhang, M.-Y., Jiang, L.-H., Huang, L., & Pang, D.-W. (2025). Triplet–triplet annihilation upconversion: From molecules to materials. *Accounts of Chemical Research*. https://doi.org/10.1021/acs.accounts.5c00403

Huang, L., Le, T., Huang, K., & Han, G. (2021). Enzymatic enhancing of triplet–triplet annihilation upconversion by breaking oxygen quenching for background-free biological sensing. *Nature Communications*, *12*(1). https://doi.org/10.1038/s41467-021-22282-1

Huang, L., Zeng, L., Chen, Y., Yu, N., Wang, L., Huang, K., Zhao, Y., & Han, G. (2021). Long wavelength single photon like driven photolysis via triplet triplet annihilation. *Nature Communications*, *12*(1). https://doi.org/10.1038/s41467-020-20326-6

Kim, Y.-J., Song, J., Lee, D.-H., Um, S. H., & Bhang, S. H. (2023). Suppressing cancer by damaging cancer cell DNA using led irradiation. *Journal of Photochemistry and Photobiology B: Biology*, *243*, 112714. https://doi.org/10.1016/j.jphotobiol.2023.112714

Naimovičius, L., Bharmoria, P., & Moth-Poulsen, K. (2023). Triplet–triplet annihilation mediated photon upconversion solar energy systems. *Materials Chemistry Frontiers*, *7*(12), 2297–2315. https://doi.org/10.1039/d3qm00069a

Park, H.-W., Choi, J.-W., Joo, K.-K., Kim, N.-R., & Shin, C.-D. (2023). Estimating fluor emission spectra using digital image analysis compared to spectrophotometer measurements. *Sensors*, *23*(9), 4291. https://doi.org/10.3390/s23094291

Scharnagl, B., Iden, S. C., Durner, W., Vereecken, H., & Herbst, M. (2015). Inverse modelling of in situ Soil Water Dynamics: Accounting for heteroscedastic, autocorrelated, and non-Gaussian Distributed Residuals. *Hydrology and Earth System Sciences Discussions*, *12*, 2155–2199. https://doi.org/10.5194/hessd-12-2155-2015

Seo, S. E., Choe, H.-S., Cho, H., Kim, H., Kim, J.-H., & Kwon, O. S. (2022). Recent advances in materials for and applications of triplet–triplet annihilation-based upconversion. *Journal of Materials Chemistry C*, *10*(12), 4483–4496. https://doi.org/10.1039/d1tc03551g

Wan, S., Wang, D., Cai, M., Shi, Y., Zhang, Y., Chen, S., Ye, C., & Song, Y. (2023). Photochemically deoxygenating micelles for protecting TTA-UC against oxygen quenching. *Chemical Communications*, *59*(93), 13895–13898. https://doi.org/10.1039/d3cc04327d

Wei, Y., Wang, Y., Zhou, Q., Zhang, S., Zhang, B., Zhou, X., & Liu, S. (2020). Solvent effects on triplet–triplet annihilation upconversion kinetics of perylene with a Bodipy-phenyl-C60photosensitizer. *Physical Chemistry Chemical Physics*, *22*(45), 26372–26382. https://doi.org/10.1039/d0cp04230g