Experiment: From Low to High: Upconversion Based on Triplet-Triplet Annihilation

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1. Introduction

Energy flows high to low. The heat flows an object with a higher temperature to an object with a lower temperature. This appears to be always true. Today, we will see an photophysical example that defies this statement.

Triplet-triplet annihilation-based upconversion is a photophysical phenomenon that converts low-energy photons to high-energy photons. The crux of this phenomenon is that we use **two low-energy photons to make one high-energy photon**.

When molecules absorb light, emission usually occurs at lower energy than absorption (Figure 1). For example, when you photo-excite molecules using blue light, emission results in green light; recall, blue light has higher energy than green light, which has higher energy than red light.

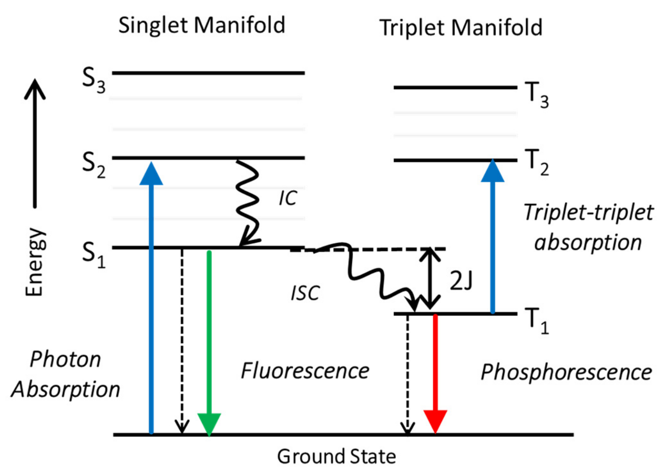


Figure 1. Jablonski diagram of typical molecules.

Upconversion converts low-energy photons using two types of *upconverter* molecules, termed *sensitizer* and *annihilator* (ref. 1) The sensitizer molecule absorbs low-energy light, and the annihilator (or emitter) molecule outputs high-energy photons. The series of energy transfer steps that these molecules progress through is shown in Figure 2. Upconversion begins with excitation of ground state sensitizer, ^0S, to the singlet excited state, ^1S, by low-energy light. ^1S proceeds to its triplet excited state, ^3S, by intersystem crossing (ISC); this process decreases the energy at first. Then, triplet-triplet energy transfer (TTET) from ^3S to the ground state annihilator, ^0A, generating the triplet excited state annihilator, ^3A. Finally, two ^3A's undergo triplet-triplet annihilation (TTA), a process that combines their energies to produce the singlet excited state annihilator, ^1A, which is remarkably high in energy compared to the original excitation light. Relaxation of these ^1A excited states results in the emission of high-energy photons. Upconversion finds applications in modern photovoltaics for this ability to salvage low-energy photons that aren't efficiently converted into energy by silicon-based solar cells, and biomedical applications such as optical sensors as we can use long wavelength light to penetrate deeper into the tissue.

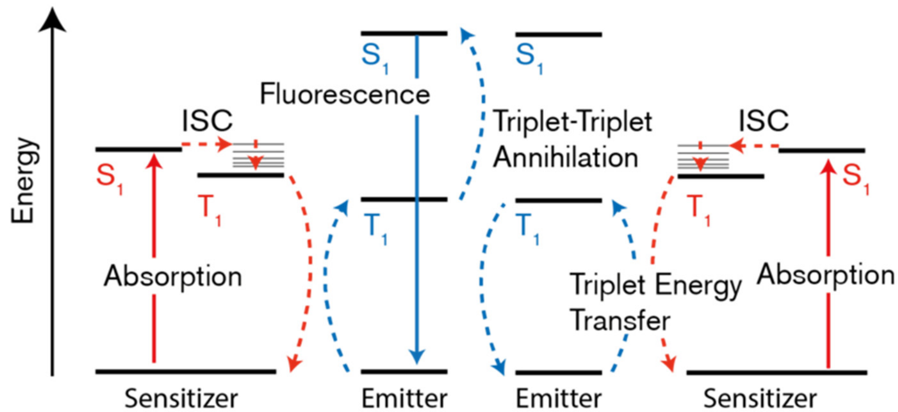


Figure 2. Jablonski diagram describing the triplet–triplet annihilation upconversion process. (1) A sensitizer absorbs a low energy photon and rapidly populates its first triplet excited state (T_1) after intersystem crossing (ISC) from the singlet excited state (S_1). (2) The triplet energy can then be transferred to an annihilator molecule through a triplet-triplet energy transfer (TTET) process, and (3) generating one triplet excited annihilator molecule. (4) When two triplet excited annihilator molecules come together they can undergo triplet–triplet annihilation, that (5) generates one singlet excited annihilator which can deactivate to its ground state by emitting a photon.

Triplet excited states of molecules can react with molecular oxygen whose ground state is triplet, resulting in the loss of energy. In other words, molecular oxygen quenches triplet excited states of sensitizer and/or annihilators before they can undergo TTET and TTA processes, therefore we don't usually observe photon upconversion under aerobic conditions. However, by using a gel matrix (Figure 3), we can circumvent this problem.

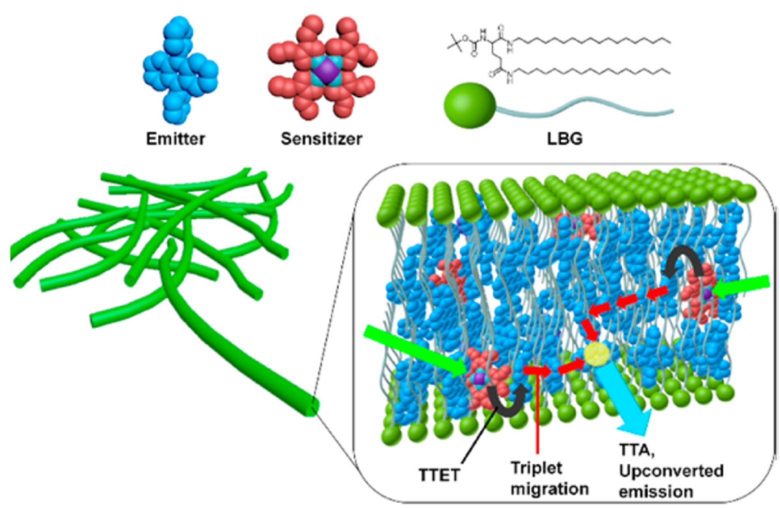


Figure 3. A schematic representation of the upconversion gel system. The figure is adopted from ref. 2.

2. Purpose

A major objective of this experiment is to give you an understanding of the nature of photon upconversion. In this experiment, we use PdOEP as a sensitizer and DPA as an annihilator (or emitter), and LGB as a gelator. See below for the structures. Using a gel matrix, you can observe TTA even under aerobic conditions (!). We can photo-excite PdOEP with a green laser. When all the processes occur as detailed in Figure 2, you will observe a blue light emission from DPA. In addition to the pairs of a sensitizer and an annihilator, you will make gels of each constituent only as well as regular fluorophore (Rhodamine 6G) to examine if you can observe upconversions, and compare the results with the pairs.

3. Experiment

Safety:

Wear gloves and goggles at all times. Prepare samples and deoxygenate in the fume hood. Carefully handle DPA, as it is a suspected carcinogen. Do not allow DMF to contact your skin, as it is an irritant. Only use the laser pointer for experimental purposes. **NEVER look directly into the laser beam** and don't shine the laser directly into the camera lens (if you take photos). DPA, PdOEP, Rhodamine 6G should be disposed of in the appropriate waste container.

Chemicals:

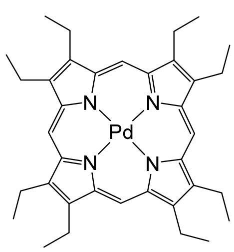
PdOEP (Premaid solution in DMF)

DPA, 6 mg (2 mg + 4 mg in tubes)

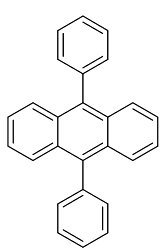
Rhodamine 6G (Premaid solution in DMF)

Gelator (LBG) (60 mg)

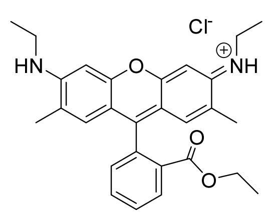
DMF = *N*,*N*-dimethylformamide



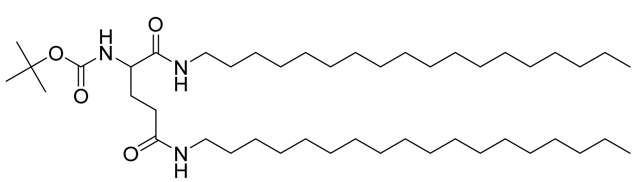
PdOEP



DPA

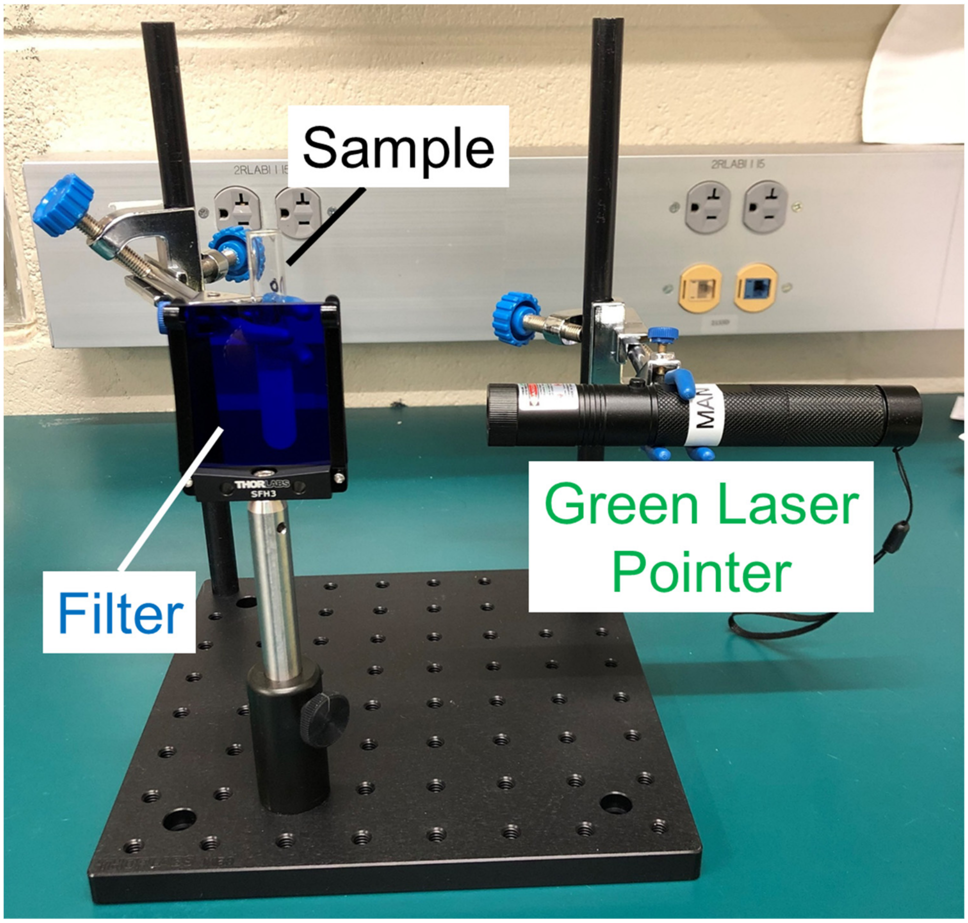


Rhodamine 6G



LBG

Optical Setup:



*We have two filters; one is blue and the other is orange/red. See Appendix for their properties.

Procedure:

1. Make the following gels:
    - **a.** Gelator only
    - **b.** DPA
    - **c.** Rhodamine 6G
    - **d.** PdOEP
    - **e.** PdOEP + DPA (2 mg)
    - **f.** PdOEP + DPA (4 mg)
2. Add the respective reagents to the test tubes.
3. Dissolve them either using 1 mL of DMF (gels **a**, **b**, **c**) or using 1 mL of PdOEP/DMF stock soluton (**d**, **e**, **f**).
4. Swirl/stir the solution until all the reagents are dissolved: solution will be cloudy so do not wait until solution is clear, just enough to remove major clumps.

5. Place a test tube in a hot water bath at 80 °C for a couple of minutes, observing the solution becoming clear during heating. Cuvette should be submerged so water line is above the solution line to ensure even heating.
6. Remove from water bath and cool to room temperature. A test tube should be suspended by the neck of the cuvette via clamps to prevent uneven cooling to the solution from being placed on a cool surface such as a table.
7. Bring the samples to one of the stations. Use the **blue** and **red** filters to see emission (if any) upon photoexcitation with the green laser. Record your observations below. You can take pictures.

	Emission with Blue Filter	Emission with Red Filter
Gel only		
DPA		
PdOEP		
Rhodamine 6G		
PdOEP + DPA (2 mg)		
PdOEP + DPA (4 mg)		

4. Some remarks and things to think about

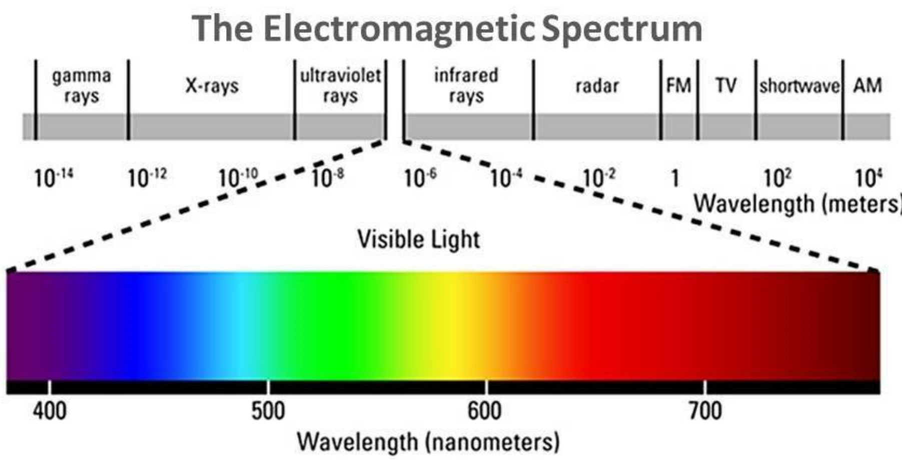
a. In which samples did you observe normal fluorescence emission (with red filter)? Why?
b. In which samples did you observe upconversion emission (with blue filter)? Why?
c. There are other combinations of sensitizer and annihilators and we can convert from red light to blue light. More quantitative analysis can be performed by using laser-based spectroscopic methods.

5. References

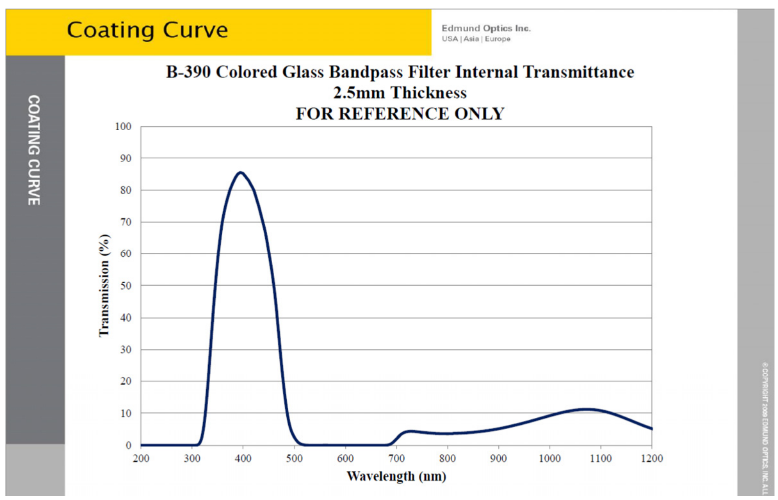
1. Singh-Rachford, T. N.; Castellano, F. N., Photon upconversion based on sensitized triplet–triplet annihilation. Coordin. Chem. Rev. **2010,** 254, 2560-2573.

2. Duan, P.; Yanai, N.; Nagatomi, H.; Kimizuka, N. Photon upconversion in supramolecular gel matrixes: Spontaneous accumulation of light-harvesting donor-acceptor arrays in nanofibers and acquired air stability. *J. Am. Chem. Soc.* **2015**, 137, 1887–1894.

6. Appendix



The Blue filter you use: (almost) only blue light (~400 nm) can transmit.



The Red filter you use: only orange/red light (> 600 nm) can transmit.