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). Researchers frequently use TTA-UC systems at their peak concentrations, providing the brightest light intensity possible. However, novel biological applications of TTA-UC demand a lower light intensity, as to not damage or stress living cells (Dou et al., 2017). The ratio between sensitizer and annihilator and its effect on the light intensity produced has not been well studied. The model created in this study reliably predicted peak light intensity from a given ratio and can provide guidance when designing TTA-UC applications for biological systems.

Sensitizer

A sensitizer is a molecule that absorbs low energy, which is usually around 650 nm, the wavelength of red light (Chou et al., 2021). 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).

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).

Quenching

Quenching, including oxygen quenching and self-quenching, refers to any reason why a TTA-UC system is unable to produce light. 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, such as nitrogen and argon (Wan et al., 2023). Self-quenching is a phenomenon in which the annihilator concentration in the system is too high in comparison to sensitizer. Unused annihilator molecules reabsorb the light that is being produced by other annihilator molecules. Thus, light is unable to escape the system (Olesund et al., 2023).

Applications

Research on TTA-UC has led to its utility in many different fields. 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 (Dou et al., 2017). 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.