

A diffusion-centric scheme for solid-state triplet-triplet annihilation upconverters

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Upconversion materials can shift spectral power density from redder to bluer wavelengths by combining several low-energy photons into a higher-energy excited state. While there are many useful technological applications for the upconversion (UC) of different light sources, photovoltaics and photocatalysis arguably dominate this space. This is because UC can reduce the lossy transmission of sunlight with energy below the band gap of a semiconductor light absorber, which contributes significantly to the low limiting efficiency of single-junction absorbers. When placed on the shaded side of a bifacial absorber, an upconverter can absorb transmitted photons and re-radiate them at energies above the absorber's band gap, sensitizing it to an otherwise-wasted portion of the solar spectrum [1].

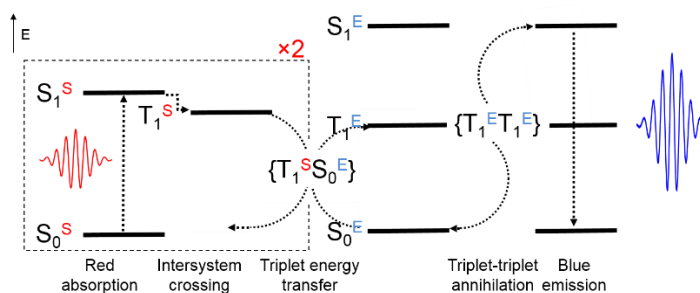


Figure 1 Energy level diagram of the TTA-UC process in a model red-to-blue upconverting solution. The sensitizer and emitter are denoted with superscripts *S* and *E*, respectively. Processes within the dashed box occur at least twice per upconverted photon generated. Curly braces denote encounter complexes.

Upconverters utilising organic molecules as the upconverting moiety function by triplet-triplet annihilation (TTA), a process in which two low-energy triplet excited states combine in an encounter complex, annihilating to yield a single higher-energy singlet state. Subsequent light emission or charge injection from this state is the culmination of the upconversion process [2]. The crucial intermediate species in TTA is a long-lived triplet excited state, denoted T_1^E . Generating this requires two chromophores working together: a sensitizer, which generates triplet excitations following light absorption, and an emitter, which accepts these triplet excitations, undergoes TTA, and releases energy from the upconverted state. An energy level diagram of the TTA-UC process is shown in fig. 1.

A simplified rate model of the TTA-UC system shown in figure 1 whilst under steady illumination is

$$k_\phi [S_0^S] = k_1 [T_1^E] + k_2 [T_1^E]^2, \quad (1)$$

where $[S_0^S]$ and $[T_1^E]$ are the concentrations of ground state sensitizer and triplet-excited emitter, k_ϕ is the sensitizer photoexcitation rate, k_1 is the rate constant for spontaneous decay of the emitter triplet, and k_2 is the rate constant of emitter TTA. Maximising decay via the TTA mechanism, and thus the quantities $[T_1^E]$ and $k_2 [T_1^E]/k_1$, is key to achieving high UC yields.

For solution-based TTA-UC systems, eq. 1 and its permutations are usually a good description of the UC process [3]. Various methods to improve UC quantum yield can be divined from this model: those focused on denser sensitizers, multiple sensitizers and plasmonic absorbers are linked to increasing $k_\phi [S_0^S]$; phonon and matrix engineering are linked to decreasing k_1 ; and attempts to improve emitter diffusion rates or employ complementary emitter species are linked to increasing k_2 .

Solid TTA-UC materials tend to be denser light absorbers, more resistant to oxygen penetration, and superior for device integration when compared to systems in organic solvents. But the propensity of the active species is to aggregate, become dull, and diminish in triplet lifetime when transplanted from liquid to solid hosts. Correspondingly, despite increasingly complex material schemes being implemented, the external quantum efficiency of solid TTA-UC materials remains generally low at terrestrial intensities [4-7]. Overcoming these problems is a challenge. Compounding the difficulties for solid-state TTA-UC materials, many of the assumptions underlying eq. 1 no longer hold true in solids, clouding the interpretation of dynamics measurements.

A directive which may guide the development of efficient UC materials is that every photoexcitation produced along the generation profile should be able to interact with every other. This ensures the threshold intensity – at which spontaneous and TTA-driven triplet decay are equally probable – occurs well below one-sun intensity. If so, a high yield of upconverted photons can be achieved at one sun, as long as the quantum yields of the other steps in the TTA-UC process are high. Succinctly, triplets should interact over a distance at least equal to l , the characteristic length of the triplet exciton generation profile. This interaction length can be defined by r , the isotropic diffusion length of triplet excitons:

$$r \sim (4D\tau)^{0.5}, \quad (2)$$

where D is the diffusion coefficient and τ is the (triplet) lifetime [8]. The length of the generation profile can be obtained from the Beer-Lambert law. Bringing l and r into parity is difficult in solutions, as solubility sets a lower limit to the values of l that can be achieved – optimistically, using current materials an absorbance of 1.0 could be achieved over a $\sim 10\mu\text{m}$ path length, ten times larger than a similarly-optimistic estimate of r for a triplet emitter diffusing in solution.

Much greater optical densities are supported in solid films than in liquids. For a polycrystalline polyacene film, l as small as $\sim 150\text{nm}$ is achievable. Of course, r is typically diminished in the solid state as Brownian motion gives way to exciton hopping, with associated opportunities for trapping; characteristic values of r are in the range of 10-50nm for these media, and seemingly no advantage has been gained [9]. But solids allow a greater degree of control over local structure than liquids. We can thus design materials that exploit gradients in triplet energy or other properties to extend r in a favorable direction, guiding triplets to a local annihilation site, and boosting its excitation rate and upconversion yield.

My discussion focuses on some of the unexpected consequences of a diffusion-centric design criteria for solid TTA-UC materials. A design that directs and extends diffusion is proposed, along with other novel features. Using this design, it may be possible to surpass the performance of liquid TTA-UC systems in an integration-friendly format. I discuss the use of this system to enhance the efficiency of photocatalytic water splitting materials.

References

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