Efficient up-conversion by triplet-triplet annihilation

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Abstract. Following experimental determination of kinetic parameters governing the up-conversion of light by triplet-triplet annihilation (TTA-UC), we develop a kinetic model to determine the conditions required for efficient up-conversion. We discuss the assumptions underpinning statistical arguments for an upper limit to TTA-UC and argue that no such limit exists.

1. Introduction
Single threshold photovoltaic convertors suffer from an inability to harvest photons of an energy less than the threshold, restricting their efficiency to about 30%.[1] One possible improvement to the single threshold device is to place an up-converting material behind the cell which can efficiently convert the low sub-threshold photons into usable light.[2] The limiting efficiency of a cell utilizing an up-conversion (UC) system is over 50% with a threshold energy of 2 eV.[3] However, using rare-earth containing phosphors, the best UC quantum efficiency recorded is $\sim 10^{-6}$.[4] Recently, a way to up-convert red light using triplet-triplet annihilation (TTA) in organic molecules has been developed.[5, 6] In TTA-UC, efficiently emitting molecules, “emitters”, are placed in their long lived triplet states through collisions with triplet sensitizer molecules. The sensitzers are chosen such that they undergo intersystem crossing from the $S_1$ state to the $T_1$ state following absorption of a low energy photon. When two triplet emitter molecules encounter another, a complex is formed which may take on singlet, triplet or quintet spin states. Due to the degeneracies of these states, they are statistically weighted, respectively, 1:3:5, such that there is only a $1/9$ statistical chance of producing a singlet encounter complex. When formed, the singlet undergoes internal conversion to a lower energy state whereby one emitter moiety is in its $S_1$ state and the other is in its ground state ($S_0$). The excited moiety then promptly fluoresces, yielding up-converted light. The general scheme is given in Figure 1. The limiting efficiency of TTA-UC is not known, but it is widely held that it cannot exceed 11%, the statistical weighting of singlet encounter complexes. However, in 2008 we showed that 28% UC efficiency is possible using a palladium tetrakisquinoxalinophyrin as the sensitizer and rubrene as the emitter.[7] Using a pulsed laser source and time-resolved spectroscopy, we measured the rate constants indicated in Figure 1. In this article, we present the kinetic model which emerged from the previous study and discuss how spin statistics and the various kinetic parameters affect the predicted TTA-UC efficiencies.
2. Kinetic Model of TTA-UC

Under continuous illumination, there is a continuous pumping of population from the $S_0$ level into the $S_1$ level of the sensitizer. This rate is given by $k_\phi = \phi \epsilon'$, where $\phi$ has units of moles of photons dm$^{-2}$s$^{-1}$, and the molar extinction coefficient, $\epsilon' = \epsilon \log(10)$, is in M$^{-1}$dm$^{-1}$. In the case of solar irradiation, the rate is given by the integral $k_\phi = \int d\lambda \rho(\lambda) \epsilon'(\lambda)$, where $\rho$ is given in moles of photons dm$^{-2}$s$^{-1}$nm$^{-1}$. The $S_1$ state of the sensitizer lives only $\sim 2$ ps as the molecules undergo intersystem crossing to $T_1$.[7]

In the following, $X$ represents the sensitizer molecules, and $Y$ represents the emitter species. The kinetics of the triplet energy transfer and triplet-triplet annihilation procedure proceed as

$$\frac{d[X]}{dt} = k_\phi[X] - k_{TET}[Y][X] - k_{nr}[X] - k_{TTA}(2[X]^2 + [Y][X]) = -\frac{d[Y]}{dt}$$
$$\frac{d[Y]}{dt} = k_{TET}[Y][X] - k_{nr}[Y] - k_{TTA}(2[Y]^2 + [X][Y]) = -\frac{d[X]}{dt}$$

where $k_{TET}$ and $k_{TTA}$ represent the rate constants for the triplet energy transfer and triplet-triplet annihilation respectively. The constants $k_p$ and $k_{nr}$ represent the total first-order decay constants for the sensitizer and emitter triplets respectively. The kinetic processes are also shown schematically in Figure 1. These equations are solved to find steady state conditions. The efficiency, $e$, is given by

$$e = 2 \frac{k_{TTA}[Y]^2}{k_\phi[X]^2}. \quad (1)$$

In all simulations, kinetic rate constants and concentrations were held at our experimental values: $[X] = 1.16 \times 10^{-4}$ M, $[Y] = 2.30 \times 10^{-3}$ M, $k_{TET} = 3.33 \times 10^8$ M$^{-1}$s$^{-1}$, $k_{TTA} = 1 \times 10^8$ M$^{-1}$s$^{-1}$, $k_{nr} = 9000$ s$^{-1}$, $k_p = 2.5 \times 10^4$ s$^{-1}$ and $k_\phi = 10$ s$^{-1}$ unless specified otherwise.

3. Results and Discussion

Our modelling reveals a threshold behaviour for efficiency as a function of $k_{TET}$ and $[Y]$. Essentially, efficient TTA-UC can proceed if $k_{TET}[Y] \gg k_p$, as seen in Figure 2. When this is satisfied, the efficiency comes down to the competition between $k_{nr}[Y]$ and $k_{TTA}[Y]^2$. We require that $k_{TTA}[Y]^2 \gtrsim k_{nr}$.

In Figure 3, a plot of photon absorption rate against photon emission rate is presented. On the double-logarithmic plot, the order of the process is revealed by the slope. Interestingly, the slope of the plot is very sensitive to the value of $k_{nr}$, the rate of spontaneous decay of emitter triplets. At high values of $k_{nr}$, say $10^4$ s$^{-1}$, the process is seen to exhibit a quadratic nature.

**Figure 1.** Kinetic scheme of TTA-UC.
across the ranges of $k_\phi$ employed here. A value of $k_\phi = 10^4 \text{s}^{-1}$ corresponds to monochromatic light intensity of about 10 W cm$^{-2}$, for the molecules employed here. Typically, sunlight would bring about $k_\phi \sim 10^{-1} \text{s}^{-1}$. The quadratic dependence of the TTA-UC across several orders of magnitude of irradiance is due to the short life of the triplet states. Where the dominant triplet decay mechanism is non-radiative, rather than TTA, the amount of up-converted light will depend quadratically on the concentration of triplets which is controlled linearly by the level of irradiation. However, where the non-radiative processes are cut-off, so that $k_\text{nr} = 0$, the process is entirely linear. In this case, triplets always have the time to react by TTA and thus the TTA-UC output is linearly dependent on the irradiation level, bringing about a slope of unity. At intermediate values of $k_\text{nr}$, the process changes smoothly from quadratic to linear as the input light is increased, as opposed to exhibiting a threshold. This behaviour has been recently observed.

It is only where the process deviates from quadratic towards linear that the TTA-UC is significantly efficient. At typical solar excitation rates of $k_\phi \sim 10^{-1} \text{s}^{-1}$, $k_\text{nr}$ must be below about 1000 s$^{-1}$ to achieve significant TTA-UC. One contaminant that likely increases $k_\text{nr}$ is dioxygen. Being a triplet ground state, when it encounters a triplet emitter molecule in solution it can undergo TTA to yield singlet oxygen and a ground state emitter, short circuiting the TTA-UC process. With concentrations of dioxygen as low as $10^{-7}$ M (one atmosphere is $10^{-7}$ M), $k_\text{nr}$ will be enhanced by a contribution on the order of 1000 s$^{-1}$. As such, dioxygen concentrations must be kept low to achieve efficient TTA. In our experiments concerning TTA-UC kinetics in degassed toluene, the measured $k_\text{nr}$ value of 9000 s$^{-1}$ is too high to achieve efficient TTA-UC under solar illumination. It is likely that our experiments were affected by trace levels of oxygen, foreshortening the lifetime of the rubrene triplet state. Nevertheless, the high efficiencies obtained under pulsed-laser illumination (28%) and the excellent agreement with our kinetic model suggests that higher efficiencies could be obtained with more careful deoxygenation.

The competition between intramolecular and intermolecular processes will be more important still when implementing TTA-UC in solid polymer films. In such environments, the rates $k_{TTA}$ and $k_{TET}$ will be reduced by a factor consistent with the increased viscosity of the environment.

Solving for a steady-state population of triplets, we find that the condition $k_{TTA}[^3Y] \gtrsim k_\text{nr}$ translates to the condition

$$\sqrt{k_{nr}^2 + 8k_\phi[^1X]k_{TTA}/k_{nr}} \gtrsim 5.$$  

(2)
4. Final remarks

Our kinetic model predicts that efficient TTA-UC can proceed providing that certain conditions are met: triplet energy must be rapidly transferred to the emitter molecules, and the emitter triplet states must be long lived with respect to the TTA rate. We find no evidence in support of a spin-statistical limitation on TTA. Indeed, our experiments, on which the present model is based, suggest that TTA can proceed with high efficiency. If quintet encounter complexes are to decay non-radiatively, rather dissociating back into triplets, the question remains: since there is no lower quintet state, to which state does the encounter complex decay? Indeed, if it does decay, then due to the energy-gap law, it is likely to decay to a state which subsequently fluoresces. The only possible quenching process is if the triplet encounter complex decays into the lower triplet state which then dissociates into a triplet and a ground state emitter. In this case the limiting efficiency is 40%.

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