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Kinetic insight into bimolecular upconversion: experiment and simulation

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We demonstrate a transient rate model for photochemical upconversion that links the internal energy transfer and triplet-triplet annihilation processes to spectroscopically measurable quantities, such as delayed fluorescence and bleaching. We confirm that our model is able to reproduce published delayed fluorescence measurements extremely well. We then use transient absorption spectroscopy to directly observe the dynamics of triplet populations through clear observation of delayed bleaching of the emitter species, providing direct evicende of triplet energy transfer from sensitiser to emitter molecules. This more complex experiment is also well reproduced by our model.

1 Introduction

Upconversion is a process in which two low energy photons are absorbed to allow one higher energy photon to be emitted. Two distinct sequential absorption processes requiring relatively low excitation intensity, a few 10s of mW, have been demonstrated in rare-earth glasses[1,2] and molecular solutions[3–5]. One demonstrated application for upconversion is enhancement of solar cell efficiency. In high band-gap solar cells, the single largest energy loss is the lack or incomplete absorption of photons with energy below the cells' band gap[6]. Upconversion addresses this loss, and has the potential to raise the fundamental power conversion efficiency limit of a single junction solar cell from 33% to 47.6%[7]. Enhanced power conversion efficiency has been experimentally realised through both rare-earth[8] and molecular[9] upconversion, where low energy photons that reach the rear of a solar cell are re-radiated at a higher energy, sufficient for the solar cell to absorb.

The molecular upconversion energy step ladder is shown in Figure 1. This method of upconverting light is particularly well suited for upconversion of the visible and near-IR wavelengths ($\gamma_1 < 700$ nm). This is because sensitising dyes exhibit strong absorption in this region, providing a good way to get energy into the system. Metallated porphyrin molecules are often employed in this role. The excitation crosses rapidly into the triplet state(T_1), typically within a few picoseconds and with an inter-system crossing (ISC) efficiency close to unity. Providing the triplet energy level of a paired fluorescent, emitting, molecule is close to that of the sensitiser's, and that there is an excess of emitter in the mixture, the sensitiser triplet is rapidly transferred to a triplet state in an emitter molecule via Dexter energy transfer[10], also known as triplet energy transfer (TET). When two triplet-excited emitter molecules interact, they can undergo a triplet-triplet annihilation (TTA) process whereby the excited singlet level of one emitter is populated and the other emitter relaxes to its ground state. This triplet-triplet annihilation process has been found to be highly efficient and while the TTA process does obey spin-selection rules, the efficiency of that process is not limited by those rules[11].

The steady state and kinetic properties of many of these emitter/sensitiser pairs have been thoroughly investigated in previous articles, for example Murakami et al.[12] recently used delayed fluorescence measurements to examine the kinetics of the final output of an upconverting system and Deng et al.[13] anlayse transient absorption measurements in the same way. Further information on fluorescent emitters and frequently used sensitisers can be found in[14–18].

2 Model

The rate model for photochemical upconversion, proposed by Auckett et al.[19], describes the dynamics of the system in terms of the rate of change of concentration of sensitiser triplets and emitter triplets and is based on empirically determined rates of energy transfer throughout the upconversion scheme. Their approach is limited to investigation the steady-state conditions

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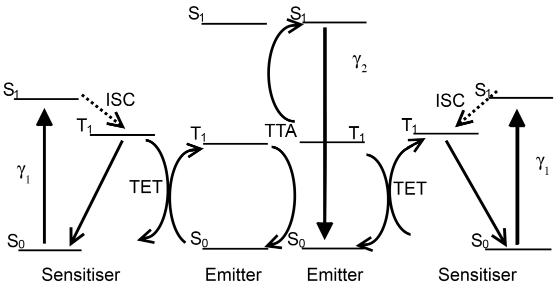

Fig. 1 Triplet-triplet annihilation upconversion schematic. Each sensitiser molecule is excited by a photon, γ_1, the excitation undergoes fast intersystem crossing (ISC) to transition into a triplet state. Triplet energy transfer (TET) the occurs between each sensitiser and an emitter. Two triplet-excited emitter molecules interact and their excitations undergo triplet-triplet annihilation (TTA). This relaxes one emitter back to its ground state and excites the other to it's S_1 state, which can then fluoresce, γ_2.

of an experiement, with our approach we are able to consider the build-up and stabilisation times as well. Our approach is also used here to probe a pulsed experiment for the first time.

For efficient upconversion, the rate constants, k, associated with the Dexter energy transfer step (k_{TET}) and the final annihilation step (k_{TTA}) must be much faster than the associated loss mechanisms. Namely phosphorescence, kp, and non-radiative decay, k_{NR}. In the model presented in this paper the two governing equations have been adapted from Aucketts work. These modified equations are presented below as equations (1) and (2), where: [ ] denotes concentration; X a sensitiser species; Y an emitter species; G and T ground and triplet states respectively; k_ϕ the flux of photons capable of exciting the sensitiser; k_p the rate of phosphorescence; k_{NR} the rate of non-radiative decay; k_{TET} the rate of triplet energy transfer and k_{TTA} the rate of triplet triplet annihilation.

$$\frac{d[X_T]}{dt} = k_\phi[X_G] - k_p[X_T] - k_{TET}[X_T][Y_G] - k_{TTA}^{XY}[X_T][Y_T] - k_{TTA}^{XX}[X_T]^2 = \frac{-d[X_G]}{dt} \qquad (1)$$

$$\frac{d[Y_T]}{dt} = k_{TET}[X_T][Y_G] - k_{NR}[Y_T] - k_{TTA}^{XY}[X_T][Y_T] - 2k_{TTA}^{YY}[Y_T]^2 = \frac{-d[Y_G]}{dt} \qquad (2)$$

We make two changes to the equations reported in[19]. We split the origional k_{TTA} terms into k_{TTA}^{XY}, k_{TTA}^{YY} and k_{TTA}^{XX} to allow for the potential differences in annihilation rates between two emitter molecules, two sensitiser molecules and that between a sensitiser and an emitter. We also remove a factor of two from the homoannihilation of sensitiser triplets term to make it $k_{TTA}[X_T]^2$. This reflects new understanding on recombination dynamics of these triplets. We make this second change as an unsuccessful annihilation event between two sensitiser molecules that does not necessarily depopulate both triplet levels: one sensitiser will be excited to a singlet state and undergo ISC once more, leaving one triplet state sensitiser and one ground state sensitiser[11]. In our experimental section we find that these changes make very little difference to the output of our model in this experimental regime. These changes only become significant at impractically high irradiance levels, and impossibly high concentrations. We make them only to provide the most correct description of the molecular dynamics possible with our current understanding.

Previous studies have used experimental techniques to calculate these rate constants, for example using steady-state and transient techniques such as delayed fluorescence or phosphorescence measurements[11]. In these experiments, the triplet concentrations must be back-calculated based on the framework of equations (1) and (2), whereas in this paper we use transient absorption spectroscopy to measure the triplet concentrations directly, as presented in the following sections.

The time-dependant rate model that was developed for this work solves the rate equations (1) and (2) numerically. This is done by using the ODE45 library in Matlab, which employs a Runge-Kutta order 4 method[20] to solve equations 1 and 2 at dynamically varying discrete time intervals (1-10 ns). This provides a time-dependent description of the population of triplet states on emitter and sensitiser molecules within the upconversion system. By choosing a constant k_ϕ and taking the values of $[X_T]$ and $[Y_T]$ at long times, i.e. once $\frac{d[X_T]}{dt} \approx \frac{d[Y_T]}{dt} \approx 0$, our model reproduces the steady-state results presented in the original model[19]. If we then include experimentally determined rate constants of a particular molecular system in the calculations, it is possible to predict or replicate steady state experimental results. Setting $k_\phi = 0$ and starting the simulation with a non-zero $[X_T]$ to simulate the effect of an excitation pulse allows even pulsed laser experiments to be modelled. This is achieved by calculating the fraction of molecules that will be excited by a laser pulse, and assuming that ISC proceeds with 100% efficiency to provide the initial value of $[X_T]$.

3 Experimental Details

By choosing the the active upconverting molecules under investigation to be the same as those in the above study[11], it is possible to validate our model in relation to previously published data. Palladium(II) tetrakisquinoxalinoporphyrin (PQ_4Pd) is the absorbing (sensitising) species and rubrene the emitter species. The structures of these molecules and the relevant optical transitions are shown in Figure 2.

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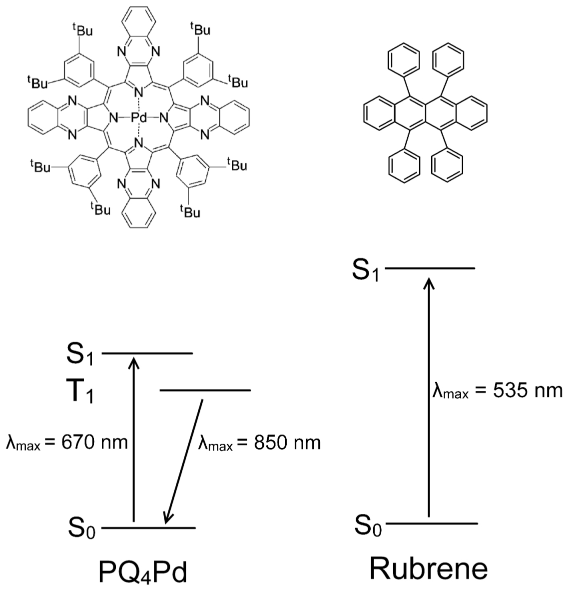

Fig. 2 Top left: Structure of Palladium(*II*) tetrakisquinoxalino porphyrin (PQ_4Pd). Top right: Structure of rubrene. Bottom: Peak optical transitions for each molecule, with λ_{max} in nm.

The PQ_4Pd was synthesised at the University of Sydney[21]. The rubrene was purchased from Sigma-Aldrich, and was used without further purification. Following dissolution in toluene to the required concentration, each solution was purged of oxygen by being left open in a nitrogen glovebox overnight. The reliability of this passive process is demonstrated here by experimentally determining the value of k_{TET} for this system and comparing it to published data[11]. We derive k_{TET} through transient absorption spectrocsopy. This is achieved by varying the concentration of rubrene in a PQ_4Pd/rubrene sample and observing the recovery time of the ground state of the porphyrin after laser excitation. The Stern-Volmer equation (3) is then used to extract the rate constant, as shown in Figure 3, where we find that there is a 2% difference between our result and that which has been published previously.

$$\frac{1}{\tau} = k_{TET}[Rubrene] + \frac{1}{\tau_0} \tag{3}$$

Transient Absorption Spectroscopy (TAS) is a pump-probe technique that allows for direct observation of excited state yields and dynamics, making it possible to understand the energy flow through a molecular upconversion system. In our experiments pump pulses were produced by a Photon Technology International GL-301 dye laser, pumped with a Photon Technology International GL-3300 Nitrogen laser source. These pulses had a pulse width of 2 ns at a repetition rate of 4 Hz. The output from a Xe lamp was passed through a monochromator to provide the probe beam. Samples were sealed in a 1 mm quartz cuvette and placed at the conjuction of the probe beam and pump pulses.

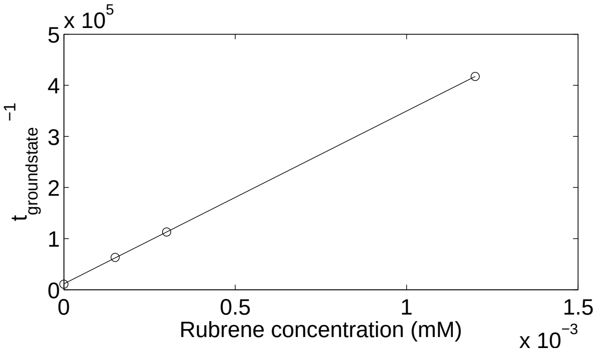

Fig. 3 Plot of reciprocal of recovery time of sensitiser ground state with varying rubrene concentration. The fitted curve is a plot of $y = k \times x + c$ where k corresponds to k_{TET} and have a value of 3.4×10^8. The value reported in[11] was 3.1×10^8.

4 Results

A plot of the reduction in population of emitter triplets after laser illumination from a selection of pulse energies is given in Cheng et al. (2010)[11]. In this paper, the authors provide the equations used to fit their data. Our rate model lends itself to the straightforward reproduction of this experiment. So we first validate our model by comparing it's result to that which has been published, as shown in Figure 4. This figure clearly has an excellent fit between the two curves, which diverge slightly only at relatively long time scales.

Pumping PQ_4Pd at its ground state absorption peak (λ = 660 nm) forms a long lived triplet state on that species. This excited state also has a characteristic absorption spectrum, shown in Figure 5. Here it can be seen that, along with the expected bleach of the PQ_4Pd ground state, there is a broad absorption feature induced between 530-600 nm, which we attribute to optical excitation up the triplet channel of the porphyrin. This PQ_4Pd specific absorption feature overlaps the ground state absorption of the rubrene emitter, also shown in Figure 5). The overlap between the excited sensitiser's induced absorbance and the ground state emitters absorbance spectrum has important implications when considering the TAS spectra of these species when mixed.

From Figure 3 we see that sensitiser triplet lifetime decreases as higher concentrations of emitter molecules are incorporated into the system. This is because a triplet quenching pathway is introduced by the emitter. The decrease in lifetime does not, in itself, provide direct evidence of TET. To provide that we must probe at the ground state absorption of rubrene,

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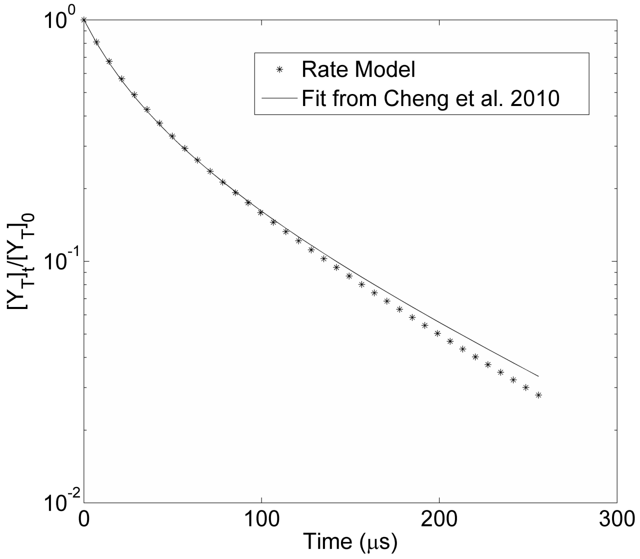

Fig. 4 Comparison of model output, stars, with a fit to experimental data from [11], solid curve.

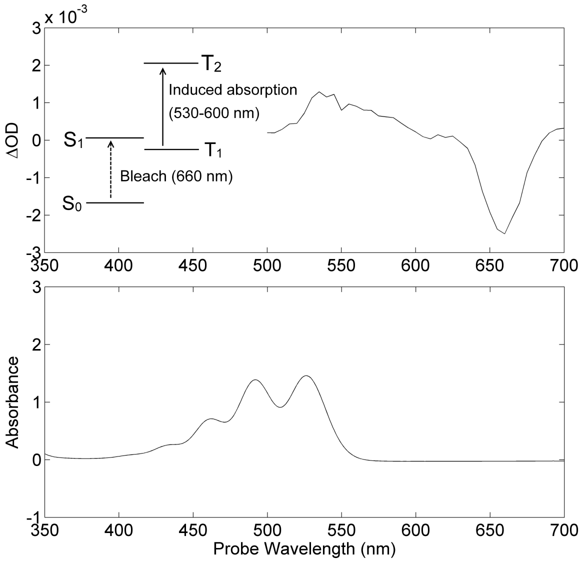

Fig. 5 Top: Transient absorption spectrum of PQ_4Pd when excited at S_0 (660 nm), 3 μs after pump excitation. Inset indicates relevant optical transitions: A bleach at 660 nm due to a reduction in population of ground state PQ_4Pd; and an induced absorption due to the increased population of PQ_4Pd triplet states. Bottom: Absorption spectrum of rubrene.

while the pump remains at 660 nm. Figure 6 shows the result of this experiment: a mixture of [0.1 mM] PQ_4Pd and [2 mM] rubrene in toluene was pumped at 660 nm, where rubrene does not absorb, and the probe wavelength was chosen as 535 nm, corresponding to the λ_{max} of ground state rubrene.

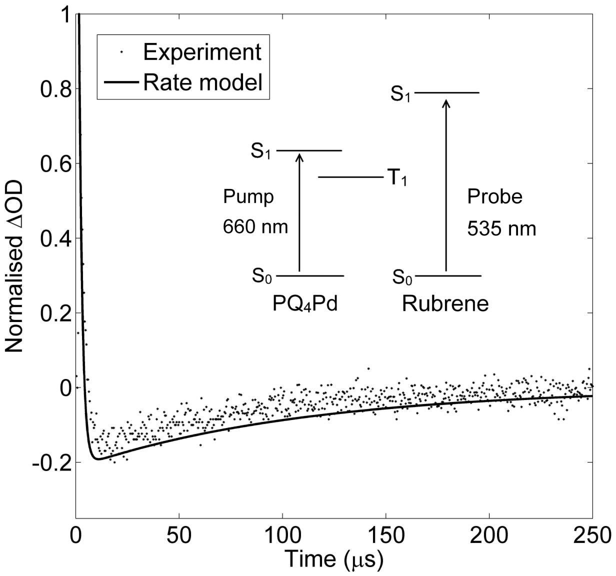

Fig. 6 Transient decay of upconverting mixture, pumped at PQ_4Pd ground state (660 nm), probed at rubrene ground state (535 nm). Dots show experimental data, solid line shows output from our rate model. Inset shows relevant optical transitions of PQ_4Pd and Rubrene, along with the pump and probe wavelengths used for this experiment.

We attribute the initial induced absorption seen in Figure 6 to the previously observed optical triplet excitation of the sensitiser, shown in Figure 5. The decay of this induced absorption proceeds at a rate comparable to the regeneration of the sensitiser ground state, as indicated in Figure 3. The delayed bleach in the rubrene ground state that follows this induced absorption then directly shows the process of triplet energy transfer from sensitiser to emitter molecules.

The solid line in Figure 6 shows the result of running our model with known experimental parameters and the published rate constants for this system as inputs[19]. The value of $\Delta\ OD$ was calculated from equation 4: where TS_{abs} is the contribution of one triplet excited sensitiser molecule to the induced absorption and GE_{abs} is the contribution of one molecule to the ground state absorbance of our emitter, or its molar extinction coefficient. These values are then normalised. The rise time of the induced absorbance is taken to be instantaneous, as the ISC process is complete within a few 10s of ps. The rate of the subsequent decay is primarily determined by two terms in equation 1: $k_p[X_T]$ and $k_{TET}[X_T][Y_G]$. As $[X_T]$ is always small, the $k^{XX}_{TTA}[X_T]^2$ term has little impact. After the delayed bleach builds, it then decays at some rate, determined by terms in equation 2: at high $[Y_T]$, the $2k^{YY}_{TTA}[Y_T]^2$ term is

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dominant, and at longer times the $k_{NR}[Y_T]$ term takes over.

$$\Delta\, OD = [X_T] \times TS_{abs} - [Y_T] \times GE_{abs} \tag{4}$$

It is clear that at each stage of the curve our rate model fits the experimental data well, showing that each regime is described by the model in a physically consistent way. The principal source of uncertainty in this calculation is the value of GE_{abs}. The probe beam produces much lower intensity at shorter wavelengths, from which GE_{abs} is derived. A more accurate measurement of GE_{abs} would not alter the dynamics of the decay curve, it would simply scale the normalised Δ OD axis.

5 Conclusions

We have modified established rate equations and solved them to produce a time-dependent rate model for a bimolecular upconversion system. Our model reproduces experimental data from both steady state modelling results[19], and delayed fluorescence experiments[11]. We have also used Transient Absorption Spectroscopy (TAS) to directly observe triplet energy transfer between sensitiser (PQ_4Pd) and emitter (rubrene) molecules in this system. We find that an initial induced absorption due to sensitiser triplets decays into the characteristic delayed bleach on the emitter ground state on the expected time scale, providing direct evidence of triplet energy transfer between the molecules. Additionally, our rate model produces a physically consistent reproduction of this TAS result, confirming that these rate equations are sufficient to describe the dynamics of molecular upconversion in solution.

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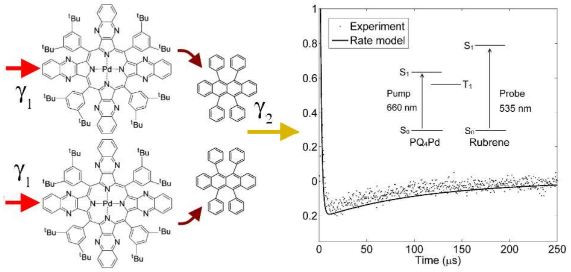
Direct observation of triplet energy transfer from sensitiser to emitter is modelled and provides comprehensive description of bimolecular upconversion.



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