

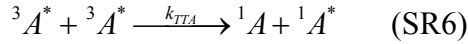
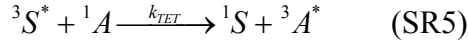
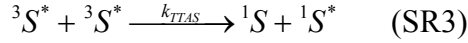
Supporting information for  
**Photon-Upconversion: Towards Solar Energy Applications**

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### Triplet-Triplet Annihilation Upconversion quantum yield

The overall upconversion process can be summarized in the following reactions:



where annihilation of both the sensitizer and annihilator have been considered but not the “hetero” annihilation between these two species. The kinetics describing the upconversion process can be described with a set of differential equations:

$$\frac{d[{}^1S]}{dt} = k_{TTAS}[{}^3S^*]^2 + k_{PS}[{}^3S^*] + k_{TET}[{}^3S^*][{}^1A] \quad (\text{S1})$$

$$\frac{d[{}^1S^*]}{dt} = k_{TTAS}[{}^3S^*]^2 - k_{isc}[{}^1S^*] \quad (\text{S2})$$

$$\frac{d[{}^3S^*]}{dt} = k_{isc}[{}^1S^*] - 2k_{TTAS}[{}^3S^*]^2 - k_{PS}[{}^3S^*] - k_{TET}[{}^3S^*][{}^1A] \quad (\text{S3})$$

$$\frac{d[{}^3A^*]}{dt} = k_{TET}[{}^3S^*][{}^1A] - 2k_{TTA}[{}^3A^*]^2 - k_{PA}[{}^3A^*] \quad (\text{S4})$$

$$\frac{d[{}^1A^*]}{dt} = k_{TTA}[{}^3A^*]^2 - k_{FA}[{}^1A^*] \quad (\text{S5})$$

$$\frac{d[{}^1A]}{dt} = k_{TTA}[{}^3A^*]^2 + k_{FA}[{}^1A^*] + k_{PA}[{}^3A^*] - k_{TET}[{}^3S^*][{}^1A] \quad (\text{S6})$$

In order to obtain the expressions for the quantum efficiencies  $\Phi_{TET}$  and  $\Phi_{TTA}$ , steady-state conditions are assumed ( $d[X]/dt = 0$ ) and the quantum efficiency is defined as the ratio of the rate of the specific process and the total rate of producing the precursor state:

$$\Phi_x = \frac{\text{rate of process X}}{\text{total rate of forming precursor state}} \quad (\text{S7})$$

Using eq. (S7) an expression for the efficiency of triplet energy transfer (reaction SR5) can be defined as the rate of this reaction,  $k_{TET}[{}^3S^*][{}^1A]$ , divided by the total rate of producing the precursor state ( ${}^3S^*$ ),  $k_{isc}[{}^1S^*]$ . Assuming steady state and using eqs. (S3) and (S4) the triplet energy transfer efficiency is

$$\begin{aligned}
\Phi_{TET} &= \frac{k_{TET}[^3S^*][^1A]}{k_{isc}[^1S^*]} = \frac{k_{TET}[^3S^*][^1A]}{k_{TET}[^3S^*][^1A] + 2k_{TTAS}[^3S^*]^2 + k_{PS}[^3S^*]} = \\
&= \frac{k_{TET}[^1A]}{k_{TET}[^1A] + 2k_{TTAS}[^3S^*] + k_{PS}}
\end{aligned} \tag{S8}$$

Similarly, an expression for the efficiency of triplet-triplet annihilation ( $\Phi_{TTA}$ ) is obtained through making the steady state assumption and using eq. (S4):

$$\begin{aligned}
\Phi_{TTA} &= \frac{k_{TTA}[^3A^*]^2}{k_{TET}[^3S^*][^1A]} = \frac{k_{TTA}[^3A^*]^2}{2k_{TTA}[^3A^*]^2 + k_{PA}[^3A^*]} = \\
&= \frac{k_{TTA}[^3A^*]}{2k_{TTA}[^3A^*] + k_{PA}}
\end{aligned} \tag{S9}$$

### Estimating Upconversion Energy Shift

In order to estimate the Upconversion Energy Shift of a Triplet-Triplet Annihilation upconversion system we suggest relying on the distance between the average integral weighted center points of the absorption and emission spectra of an optimally composed sensitizer-annihilator assembly. This method gives a more fair measure of upconversion energy as it takes in to consideration the shape and density of the absorption and emission spectra of the system as a whole. In this way any possible change in absorption and emission spectra of the overall system resulting from an interaction of the two components is taken into account.

Firstly, the wavelength ( $\lambda$ ) scale of the spectrum is converted to wavenumbers ( $\nu$ ) by taking the reciprocal and the intensity is corrected<sup>1</sup> as

$$I(\nu) = \lambda^2 I(\lambda) \quad (\text{S10})$$

For the upconverted emission spectrum from the annihilator, the lower  $\nu_L^A$  (blue side) and upper  $\nu_U^A$  (red side) integral limits should be set to the beginning and end of the upconversion emission, respectively. In the case that the upconversion emission and sensitizer emission overlap to the degree where it is not possible to locate an end to the upconversion emission in a reliable way, one should directly excite the annihilator in the same optimally composed system and use that directly excited annihilator emission to locate the end of the emission spectrum (red side). The weighted upconversion emission center is then given by

$$\bar{\nu}_W^A = \frac{\int_{\nu_L^A}^{\nu_U^A} E^A(\nu) \nu d\nu}{\int_{\nu_L^A}^{\nu_U^A} E^A(\nu) d\nu} \quad (\text{S11})$$

in wavenumbers.

The weight averaged absorption spectrum center of the sensitizer should be obtained by setting the lower integral limit (blue side) to the weighted upconversion emission center ( $\nu_L^S = \bar{\nu}_W^A$ ) and the upper integral limit  $\nu_U^S$  to the end of sensitizer absorption towards the red region. Similarly to equation (S11) the weighted absorption center of the sensitizer in the presence of the annihilator is given by

$$\bar{\nu}_W^S = \frac{\int_{\nu_L^S = \bar{\nu}_W^A}^{\nu_U^S} A^S(\nu) \nu d\nu}{\int_{\nu_L^S = \bar{\nu}_W^A}^{\nu_U^S} A^S(\nu) d\nu} \quad (\text{S12})$$

in wavenumbers. The two obtained center wavelengths  $\bar{\nu}_W^A$  and  $\bar{\nu}_W^S$  are converted to energy (eV) and the difference between them is given as a measure of **Upconversion Energy Shift (UES)**.

Finally it is suggested to provide, at least in supporting information, a complete individual absorption and emission spectrum of the sensitizer and annihilator as well as for an optimized system of the two. The integral limits ( $\nu_L^A, \nu_U^A, \nu_U^S$ ) as well as the weighted center wavelengths ( $\bar{\nu}_W^A, \bar{\nu}_W^S$ ) should be illustrated in the graph.

## References

1. J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Springer Science, New York, third., 2006