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Correction: Extracting accurate information from triplet–triplet annihilation upconversion data with a mass-conserving kinetic model

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Correction for 'Extracting accurate information from triplet–triplet annihilation upconversion data with a mass-conserving kinetic model' by Abhishek Kalpattu *et al.*, *Phys. Chem. Chem. Phys.*, 2022, **24**, 28174–28190, <https://doi.org/10.1039/D2CP03986A>.

The authors would like to make the changes described below to their published article. The corrected supplementary information is provided in the modified Supplementary Information published alongside the original published article.

In the published article, the upconversion quantum yield, Φ_{UC} , was calculated using the quadratic model, and the steady-state rate of excitation in the system was approximated as $k_{ex}I[S]_0$. However, saturation occurs at high irradiance, and so the steady-state rate of excitation should instead have been given by $k_{ex}I[S]_{SS}$. In other words, the quartic model should be used in the high irradiance limit, because in the saturation regime the concentration of ground-state sensitizers available to absorb light is considerably smaller than the initial concentration of sensitizers. The major conclusions of the published paper remain unchanged, but here we correct some details regarding the behavior of Φ_{UC} at high irradiance.

As shown in the new Fig. 6, when the quartic model is used, Φ_{UC} does not decrease upon the onset of saturation; rather the rate of increase in Φ_{UC} with respect to irradiance decreases until the maximum value for Φ_{UC} is reached as $I \rightarrow \infty$. This behaviour arises at high irradiance because the rate of excitation and F_{SS} both saturate. As a result, Φ_{UC} continues to approach an asymptote with increasing irradiance even after the onset of saturation. The conclusions regarding Φ_{UC} should be modified as follows:

1. On page 28182, “Because F_{SS} is proportional to $I^{n(I)}$, we can conclude that Φ_{UC} must be proportional to $I^{n(I)-1}$.” should be replaced with “Because F_{SS} is proportional to $I^{n(I)}$, we can conclude that Φ_{UC} must be proportional to $I^{n(I)-q(I)}$, where $q(I) =$

$\frac{d(\log(k_{ex}I[S]_{SS}))}{d(\log(I))}$ is the local slope of a log–log plot of the sensitizer excitation rate as a function of irradiance. Far below the saturation regime, $q(I)$ has a value of unity.”

2. On page 28182, “When $n(I)$ is unity, $\Phi_{UC} \propto I^0$. The TTA-UC quantum yield reaches its maximum value at this irradiance, and decreases at higher irradiances.” should be replaced with “ Φ_{UC} grows slowly with I as both $n(I)$ and $q(I)$ fall below unity, and Φ_{UC} becomes independent of I as $n(I)$ approaches 0.”

3. On page 28182, “Thus, for any TTA-UC system, peak performance is achieved when the relationship between F_{SS} and I becomes strictly linear. As $n(I)$ approaches 0, Φ_{UC} becomes inversely proportional to I . As a result, Φ_{UC} decreases at irradiances high enough to saturate the intensity of upconverted fluorescence.” should be removed, although this statement holds true in the context of the external quantum yield (*vide infra*).

4. On page 28183, “As shown in Fig. 6b and d, the slope for the quantum yield of the data in Fig. 6a and c undergoes a smooth transition from a value of 1 at low irradiance, to a value of 0 when $n(I)$ is 1, and then finally to a value of -1 at high irradiances.”

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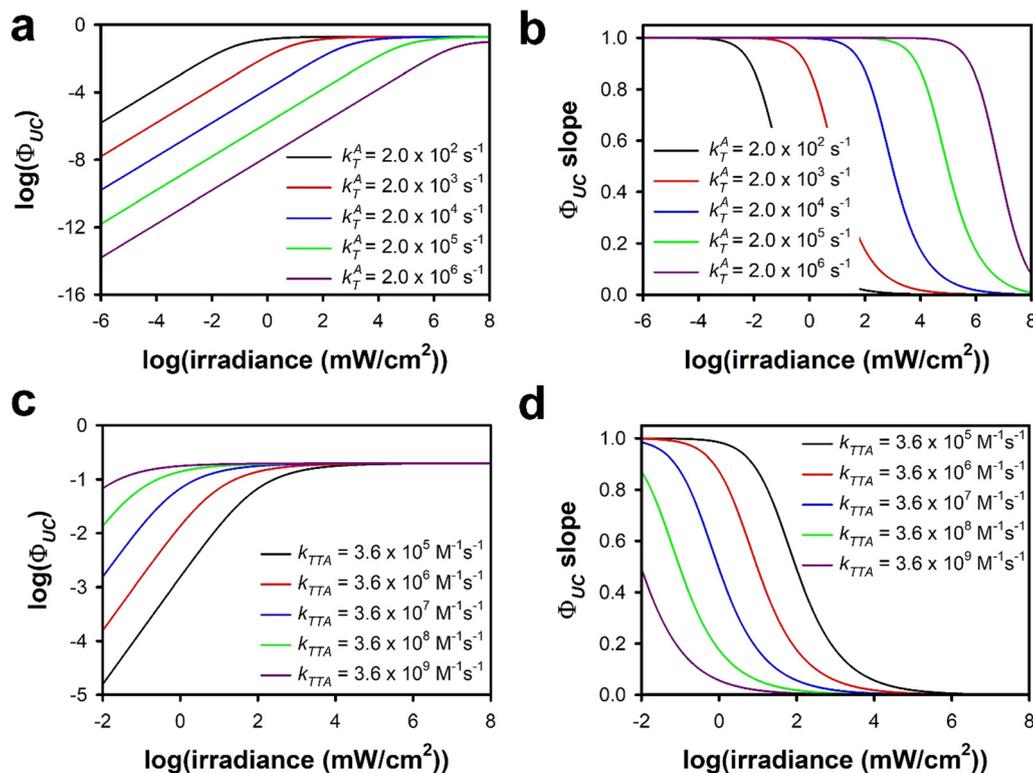


Fig. 6 The dependence of the upconversion quantum yield and its slope on irradiance for (a) and (b), respectively, different values of k_T^A , and (c) and (d), respectively, different values of k_{TTA} . See Table S1 for the values of the other parameters.

should be replaced with “As shown in Fig. 6b and d, the slope for the quantum yield of the data in Fig. 6a and c undergoes a smooth transition from a value of 1 at low irradiance to a value of 0 as $n(I)$ approaches 0.”

5. On page 28184, the value of $\Phi_{UC,max}$ in the discussion for the system with a $k_T^A = 2 \times 10^2 \text{ s}^{-1}$ should be changed from 99.5% to 99.7%. The value for $\Phi_{UC,max}$ for the system with $k_T^A = 2 \times 10^4 \text{ s}^{-1}$ should be changed from 99.6% to 99.5%. The value for $\Phi_{UC,max}$ for the system with $k_T^A = 2 \times 10^6 \text{ s}^{-1}$ should be changed from 51% to 81.7%.

Φ_{UC} values in Fig. S8, S9, S11 and S12 were also corrected. The discussion in the main text regarding Fig. S8 and S9 is correct, because the trend in Φ_{UC} and $\bar{\Phi}_{UC}$ as $n(I)$ decreases from a value of 2 to a value of 1 is unchanged. Similarly, the main trends in Fig. S11 and S12 remain the same.

To provide further insight into the behaviour of Φ_{UC} upon the onset of saturation, in Fig. S22 we show the trends in $n(I)$ and $q(I)$ when $k_T^A = 2 \times 10^2 \text{ s}^{-1}$ and when $k_T^A = 2 \times 10^5 \text{ s}^{-1}$. Φ_{UC} attains its maximum value when $n(I) = q(I)$. When $k_T^A = 2 \times 10^2 \text{ s}^{-1}$, the $n(I)$ curves overlap completely once $n(I)$ is unity (the irradiance at which $n(I) = 1$ is indicated by the vertical dotted line). However, when $k_T^A = 2 \times 10^5 \text{ s}^{-1}$, $n(I) > q(I)$ when $n(I) = 1$, and the $q(I)$ and $n(I)$ curves only converge as $n(I)$ approaches 0. The precise point at which Φ_{UC} becomes independent of I , and hence is maximized, is when $n(I) = 0$. However, for ideal TTA-UC systems, Φ_{UC} is close to $\Phi_{UC,max}$ at the irradiance for which $n(I) = 1$.

From a practical perspective, the external quantum efficiency $\Phi_{UC,ext}$ (the ratio of the steady-state rate of fluorescence emission, F_{SS} , to the rate of exposure to photons) is more important than the internal quantum efficiency that we treated in this article. $\Phi_{UC,ext}$ necessarily decreases in the saturation regime, as there are fewer ground-state sensitizers available to absorb photons. In the original article we expressed Φ_{UC} as $F_{SS}/k_{ex}[S]_0$. Multiplying this quantity by $h\omega_{ex}k_{ex}[S]_0/A$, where A is the area of the excitation beam and ω_{ex} is the frequency of the excitation light, gives $\Phi_{UC,ext}$. Thus, with this factor, the Φ_{UC} values in the original Fig. 6a, c and Fig. S8, S9, S11 and S12 can be converted to the correct corresponding $\Phi_{UC,ext}$ values. Fig. 6b and d in the original paper are correct if Φ_{UC} is replaced with $\Phi_{UC,ext}$ in the title of the y-axis. Please refer to revised version of the ESI (<https://doi.org/10.1039/D2CP03986A>) for the corrected S8, S9, S11 and S12 figures.

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The Royal Society of Chemistry apologises for these errors and any consequent inconvenience to authors and readers.

