Electronic Supplementary Information for

Cascade Sensitization of Triplet-triplet Annihilation based Photon Up-conversion at Sub-solar Irradiance

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1. Absorptance

We define as the absorptance \( \tilde{\alpha} \) the percentage of the incident photons that are absorbed by a molecule. In detail,

\[
\tilde{\alpha} = \frac{\text{#absorbed photons}}{\text{#incident photons}}.
\]  

(Eq. S1)

It should be noticed that the definition of \( \tilde{\alpha} \) is correlated to the transmittance \( T \) of the sample and consequently to its absorbance \( A_{\text{bs}} \):

\[
\tilde{\alpha} = 1 - T = 1 - 10^{-A_{\text{bs}}}.
\]  

(Eq. S2)

Fig. S1 enlightens the relationship between the values in Eq. S2 for the two sensitizers we used in our work. Optical absorption spectra were recorded by a Varian Cary 50 spectrometer at normal incidence in dual beam mode, with a spectral resolution of 1 nm.

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**Fig. S1** Relationship between absorbance \( A_{\text{bs}} \), transmittance \( T \) and absorptance \( \tilde{\alpha} \) for the sensitizer (PdPh\(_4\)TBP 10\(^{-4}\) M) plus the sensitizer-of-the-sensitizer (Rh640 5×10\(^{-5}\) M) mixture we used in our work in a 0.1 cm thick quartz cuvette. a) Absorbance of PdPh\(_4\)TBP (red line), Rh640 (black line) and the PdPh\(_4\)TBP+Rh640 solution (blue line). The blue solid line is the sum of the absorbance of the two molecules. b) Transmittance spectrum (blue line), i.e. the percentage of incident light transmitted by the molecules, and absorptance (red line), which is calculated by using Eq. S2, of the PdPh\(_4\)TBP+Rh640 solution.
2. Modelling the cascade-sensitized TTA-UC (csTTA-UC)

In this section, we describe the details of the derivation of the gain factor \( \eta \) reported in Eq. 5 of the main text. We defined \( \eta \) as the ratio between the number of up-converted photons in the csTTA-UC system \( N_{cs} \) and that one in the reference TTA-UC system \( N \) under the same excitation intensity:

\[
\eta = \frac{N_{cs}}{N}. \tag{Eq. S3}
\]

We can write the number of upconverted photons in the reference TTA-UC system as the product of the number of excited sensitizer S \( N_0 \), the ISC and ET efficiencies \( \phi_{ISC} \) and \( \phi_{DX} \) and the UC yield \( QY_{uc} \):

\[
N = N_0 \times \phi_{ISC} \times \phi_{DX} \times QY_{uc}. \tag{Eq. S4}
\]

Since in optimized TTA-UC systems the ISC and ET efficiencies are 100\%, the expression for \( N \) can be simplified to

\[
N = N_0 \times QY_{uc}. \tag{Eq. S5}
\]

We now consider the csTTA-UC case under the same excitation intensity, where the number of excited sensitizers-of-the-sensitizer (SS) is \( N_{SS} = \Omega N_0 \). We observe that after the light absorption the system is composed of \( N_0 \) excited S molecules and \( \Omega N_0 \) excited SS molecules. The \( F_S \) efficiency is \( \phi_{F_S} \) and it only depends on the sensitizer concentration, which has been fixed. A fraction \( \phi_{F_S} \) of the \( \Omega N_0 \) excited SS molecules transfers its energy to the sensitizers. The \( (1 - \phi_{F_S}) \) molecules can decay radiatively with a quantum yield \( \phi_{SS} \). Therefore, S can reabsorb some of the photons emitted by SS due to the superposition of its absorption and the SS fluorescence spectra. The fraction of re-absorbed photons \( \beta \) is defined as follows:

\[
\beta = \int I_{SS} \varepsilon_S d\lambda, \tag{Eq. S6}
\]

where \( I_{SS} \) is the normalized SS fluorescence intensity and \( \varepsilon_S \) is the absorptance of S. Therefore, the number of excited S molecules after the energy transfer from SS and the reabsorption of SS fluorescence is:
\[ N^1 = N_0 \left[ 1 + \Omega \left[ \phi_{F_s} + (1 - \phi_{F_s}) \phi_{SS} \right] \right] = N_0 \left[ 1 + \Omega \left( \phi_{F_s} + \Theta \right) \right] = N_0 (1 + \Omega \xi_1). \]  

(Eq. S7)

We defined \( \xi_1 \) as the sum of the Förster ET contribution, \( \phi_{F_s} \), and of the reabsorption to the re-excitation of super-sensitizers, \( \Theta \).

Because in optimized TTA-UC the Dexter transfer efficiency from sensitizers to emitters is \( \phi_{DT} = 100\% \), there are \( N^1 \) triplet-excited \( E \) molecules undergoing the TTA. The singlet-excited \( E \) molecules generated after TTA are \( N_{TT} = \frac{1}{2} N^1 f_{TT} \). Therefore, if the \( F_s \) yield is \( \phi_{F_s} \) and the emitter \( QY \) is \( \phi_E \), the number of up-converted photons after this first step is

\[ N_{cs}^1 = \frac{1}{2} N^1 f_{TT} (1 - \phi_{F_s}) \phi_E = N^1 \times QY_{uc} \times (1 - \phi_{F_s}). \]  

(Eq. S8)

The term \( (1 - \phi_{F_s}) \) in Eq. S8 points out that some of the SS molecules are being re-excited stealing energy from the emitters and restart the \( cs \) TTA-UC process as described above. The number of the SS molecules that are re-excited is

\[ N_{TT}(\phi_{F_s}^\ddagger + (1 - \phi_{F_s}^\ddagger) \phi_E) = N_{TT}(\phi_{F_s}^\ddagger + \Theta) = N_{TT} \xi_2. \]  

(Eq. S9)

Similarly as before, \( \xi_2 \) includes both the Förster ET contribution, \( \phi_{F_s}^\ddagger \), and the reabsorption \( \Theta^\ddagger \). \( \gamma \) is defined as:

\[ \gamma = \int l E \xi_{SS} d\lambda, \]  

(Eq. S10)

where \( l E \) is the normalized emitter fluorescence and \( \xi_{SS} \) is the absorptance of SS. By applying the same considerations as before, we can write the expressions for the number of excited sensitizers \( (N^2) \) and for the number of up-converted photons \( (N_{cs}^2) \) at the second step:

\[ N^2 = (N_{TT} \xi_2) \xi_1, \]  

(Eq. S11)

\[ N_{cs}^2 = \frac{1}{2} N^2 f_{TT} (1 - \phi_{F_s}^\ddagger) \phi_E = N^2 \times QY_{uc} \times (1 - \phi_{F_s}^\ddagger). \]  

(Eq. S12)
We demonstrated that the excited super-sensitizers can re-populate sensitizer molecules in a recursive process. Therefore we can write the general form of the term \( N^{(i)} \) as

\[
N^{(i)} = N^1 \left( \frac{1}{2} f \Phi_{TT} \xi_1 \xi_2 \right)^i, \tag{Eq. S13}
\]

and of the number of the total up-converted photons:

\[
N_{ex} = \sum_{i=0}^{n} N^{(i)} \frac{1}{2} f \Phi_{TT} (1 - \Phi_{F_2}) \Phi_E = \sum_{i=0}^{n} N^{(i)} \times QY_{UC} \times (1 - \Phi_{F_2}) \tag{Eq. S14}
\]

Since all the terms in Eq. S13 are lower than 1, for \( i \rightarrow \infty \) Eq. S14 is a geometric series that converges to:

\[
N_{ex} = N_0 \times QY_{UC} \times (1 - \Phi_{F_2}) \times (1 + \Omega \xi_1) \times \left( 1 - \frac{QY_{UC}}{\Phi_E} \xi_1 \xi_2 \right)^{-1} \tag{Eq. S15}
\]

in which we substituted \( N^* = N_0 (1 + \Omega \xi_1) \) as shown in Eq. S7. Combining Eq. S3, S5 and S15 yields the relation for the gain factor \( \eta \):

\[
\eta = (1 - \Phi_{F_2}) \times (1 + \Omega \xi_1) \times \left( 1 - \frac{QY_{UC} \xi_1 \xi_2}{\Phi_E} \right)^{-1}. \tag{Eq. S16}
\]
3. Relative QY measurements

We define the photoluminescence quantum yield (QY) of a molecule the ratio between the emitted and the absorbed photons. The most common way to measure it for a compound is by the use of a standard with a known QY in a dilute solution. The equation commonly employed to measure an unknown QY is:

\[
QY_x = QY_{std}\left(\frac{A_{std}}{A_x}\right)\left(\frac{I_x}{I_{std}}\right)\left(\frac{n_{std}}{n_x}\right)^2,
\]

(Eq. S17)

where \(QY_{std}\) is the QY of the reference standard. \(A_{std}\) and \(A_x\) are the number of absorbed photons of the reference and the investigated samples, respectively. \(I_{std}\) and \(I_x\) are the total integrated area of the photoluminescence (PL) emission of the reference and the investigated sample and \(n_{std}\) and \(n_x\) are the refractive indexes of the solvent in the two cases. To consider reliable the QY measurement performed with Eq. S17 there are several necessary conditions to be applied. First, the PL intensity of each sample has to be directly proportional to the absorbed light. Moreover, all geometrical factors must be identical and reflection losses must be the same for both samples. Finally, the excitation beam must be monochromatic. The diluted solution condition is crucial because in this way it is possible to avoid aggregation, reabsorption and reemission effects. Furthermore, if the sample is too concentrated the absorption event takes place only in the front surface of the sample, invalidating Eq. S17. As a rule of thumb, the samples are generally prepared to have an absorptance lower than 20-30%.

To measure the Rh640 QY we used as a standard sample a \(3\times10^{-5}\) M solution of Rhodamine 6G in Ethanol. This solution has a QY=86%. With Eq. S18 we calculated that for the Rhodamine 640 in a THF:MeOH 2:1 solution, QY=45%.
Fig. S2 Absorption (black line) and Photoluminescence spectra (blue, red lines) for (a) Rhodamine 6G $3 \times 10^{-5}$ M in EtOH and (b) Rhodamine 640 $10^{-4}$ M in THF:MeOH 2:1, respectively.

We used Eq. S17 to estimate the $c_s$TTA-UC QY. The addition of the Rh640 in the optimal concentration ($5 \times 10^{-5}$ M) allows to enhance the total absorptance of the system of a factor 2 respect to the reference TTA-UC. To simulate broadband absorption of white light, we simultaneously used two lasers (at 532 nm and at 635 nm) each exciting the sample with the same number of photons ($\sim 10^{17}$ photons cm$^{-2}$ s$^{-1}$). By considering that the number of emitted photons in $c_s$TTA-UC in this conditions increases of a factor $\sim 1.2$ respect to the reference TTA-UC, and using the $n$ values reported in (Parveen 2009), Eq. S17 becomes

$$QY_{cs} = \frac{QY_{uc}}{A_{ssc} \left( \frac{A_{ssc}}{A_{uc}} \right) \left( \frac{n_{uc}}{n_{ssc}} \right)^2} = 0.33 \left( \frac{1.2I_{uc}}{I_{uc}} \right)^2 \left( \frac{n_{uc}}{n_{ssc}} \right)^2 = \sim 18\% \quad \text{(Eq. S18)}$$

The standard $s$TTA-UC system taken as reference for this experiment is composed of PdPh$_4$TBP ($10^{-4}$ M) and perylene ($10^{-3}$ M) shows a $QY_{uc}=33\%$ under 20 suns of excitation intensity (ref. 32 in the main text). All the recorded spectra have been corrected for the setup’s optical response. All the solutions has been prepared and sealed in controlled nitrogen atmosphere using a glove box, with an oxygen concentration < 0.1 ppm.
4. Calculation and Measurements of Förster ET efficiencies

The relation for shown in Eq. S16 is critically dependent on the energy transfer efficiencies between the three chromophores composing the csTTA-UC system. As said before, for the optimized TTA-UC system composed of PdPh₄TBP and perylene we have \( \phi_{D,x}=100\% \). However, \( \phi_{FS}' \) and \( \phi_{FS}'' \) are unknown and depend only on the ET acceptor concentration, i.e. the sensitizer and SS respectively.

The energy transfer efficiency from an energy donor (D) to an energy acceptor (A) can be expressed as:

\[
\phi_{ET}(C_A) = \frac{k_{DA}(C_A)}{k_{D,0} + k_{DA}(C_A)}
\]

(Eq. S19)

\[
= 1 - \frac{I_D(C_A)}{I_{D,0}},
\]

(Eq. S20)

where \( k_{D,0} \) is the spontaneous decay rate of the donor molecule and \( k_{DA} \) is the ET rate from D to A, dependent on the acceptor concentration \( C_A \). \( I_{D,0} \) and \( I_D \) are the PL intensities of the donor in absence and in presence of the acceptor, respectively, with the latter clearly dependent on \( C_A \).

To calculate the \( FS' \) efficiency we used the relation expressed in Eq. S20, by wavelength-resolved PL measurements in a series of Rh640 samples with increasing concentration of PdPh₄TBP (from \( 10^{-8} \) M to \( 10^{-3} \) M) compared with a Rh640 sample with no PdPh₄TBP (Fig. S3). Fig. S3 shows that for our system the \( FS' \) efficiency is 45%.

![Graph showing \( FS' \) efficiency as a function of the S concentration. The coloured dots show the experimental values as calculated with Eq. S20 from \( C_S=10^{-8} \) M (yellow dot) to \( C_S=10^{-3} \) M (dark red dot). The black dashed line shows the ET values.](image-url)
predicted by Eq. S22. The inset shows the SS PL intensity measured with increasing S concentration (from $C_{S}=10^{-8}$ M to $C_{S}=10^{-3}$ M) and without sensitizer.

To calculate the $F_s^+$ yield we used the relation expressed in Eq. S19, by time-resolved PL decay measurements on a series of perylene samples with increasing concentration of Rh640 (from $10^{-7}$ M to $10^{-2}$ M) compared with a sample with no Rh640 (Fig. S4).

![Graph](image)

**Fig. S4** $F_s^+$ efficiency as a function of the SS concentration. The coloured dots show the experimental values as calculated with Eq. S20 from $C_{SS}=10^{-7}$ M (bright blue dot) to $C_{SS}=10^{-2}$ M (dark blue dot). The black dashed line shows the ET values predicted by Eq. S22. The inset shows the emitter PL decay time measured with increasing SS concentration (from $C_{SS}=10^{-7}$ M to $C_{SS}=10^{-2}$ M) and without SS.

Once the $F_s^+$ rate $k_{DA}$ has been calculated for the given concentration, we estimated the Förster radius $R_0$ from the relation:

$$\frac{k_{DA}}{k_0} = \frac{4}{3} \pi R_0^6 a^{-3} \rho_A.$$  \hspace{1cm} (Eq. S21)

$a$ is the minimum distance between the donor and the acceptor molecules and $\rho_A = N \times C_A$ is the acceptor density, where $N$ is the Avogadro number and $C_A$ is the acceptor concentration.

From Eqs. S19 and S21 it is possible to express the $F_s^+$ efficiency as a function of $C_{SS}$:

$$\phi_{F_s} = \frac{4}{3} \pi R_0^6 a^{-3} \rho_A \frac{1 + \frac{4}{3} \pi R_0^6 a^{-3} \rho_A}{1 + \frac{4}{3} \pi R_0^6 a^{-3} \rho_A}.$$  \hspace{1cm} (Eq. S22)
From Eq. S22 it is possible to calculate the $F_s$ efficiency for any $C_{ss}$. 