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 $\bar{\alpha}$ the percentage of the incident photons that are absorbed by a molecule. In detail,

$$\bar{\alpha} = \frac{\#absorbed\ photons}{\#incident\ photons}. \qquad \text{(Eq. S1)}$$

It should be noticed that the definition of $\bar{\alpha}$ is correlated to the transmittance T of the sample and consequently to its absorbance Abs:

$$\bar{\alpha} = 1 - T = 1 - 10^{-Abs}. \qquad \text{(Eq. S2)}$$

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.

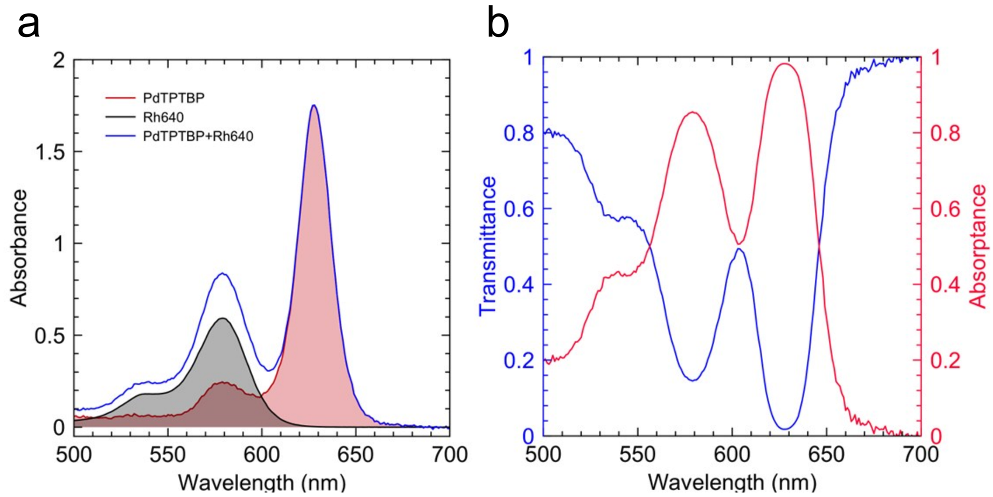

Fig. S1 Relationship between absorbance Abs, transmittance T and absorptance $\bar{\alpha}$ for the *sensitizer* ($PdPh_4TBP$ 10^{-4} M) plus the sensitizer-of-the-sensitizer (Rh640 5×10^{-5} M) mixture we used in our work in a 0.1 cm thick quartz cuvette. a) Absorbance of $PdPh_4TBP$ (red line), Rh640 (black line) and the $PdPh_4TBP$+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 $PdPh_4TBP$+Rh640 solution.

2. Modelling the cascade-sensitized TTA-UC (*cs*TTA-UC)

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

$$\eta = \frac{N_{cs}}{N}. \qquad \text{(Eq. S3)}$$

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 (ϕ_{ISC} and ϕ_{Dx}) and the UC yield (QY_{uc}):

$$N = N_0 \times \phi_{ISC} \times \phi_{Dx} \times QY_{uc}. \qquad \text{(Eq. S4)}$$

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

$$N = N_0 \times QY_{uc}. \qquad \text{(Eq. S5)}$$

We now consider the *cs*TTA-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 ΩN_0 excited SS molecules. The Fs' efficiency is ϕ'_{Fs} and it only depends on the sensitizer concentration, which has been fixed. A fraction ϕ'_{Fs} of the ΩN_0 excited SS molecules transfers its energy to the sensitizers. The $(1 - \phi'_{Fs})$ molecules can decay radiatively with a quantum yield ϕ_{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 β is defined as follows:

$$\beta = \int I_{SS} \varepsilon_S d\lambda , \qquad \text{(Eq. S6)}$$

where I_{SS} is the normalized SS fluorescence intensity and ε_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:

$$N^1 = N_0\{1 + \Omega[\phi'_{Fs} + (1 - \phi'_{Fs})\phi_{SS}\beta]\} = N_0[1 + \Omega(\phi'_{Fs} + \Theta')] = N_0(1 + \Omega\xi_1). \qquad \text{(Eq. S7)}$$

We defined ξ_1 as the sum of the Förster ET contribution, ϕ'_{Fs}, and of the reabsorption to the re-excitation of super-sensitizers, Θ'.

Because in optimized TTA-UC the Dexter transfer efficiency from sensitizers to emitters is ϕ_{Dx}=100%, there are N^1 triplet-excited E molecules undergoing the TTA. The singlet-excited E molecules generated after TTA are $N_{TT} = \frac{1}{2}N^1 f\phi_{TT}$. Therefore, if the Fs'' yield is ϕ''_{Fs} and the emitter QY is ϕ_E, the number of up-converted photons after this first step is

$$N^1_{cs} = \frac{1}{2}N^1 f\phi_{TTA}(1 - \phi''_{Fs})\phi_E = N^1 \times QY_{uc} \times (1 - \phi''_{Fs}). \qquad \text{(Eq. S8)}$$

The term $(1 - \phi''_{Fs})$ 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

$$N_{TT}(\phi''_{Fs} + (1 - \phi''_{Fs})\phi_E\gamma) = N_{TT}(\phi''_{Fs} + \Theta'') = N_{TT}\xi_2. \qquad \text{(Eq. S9)}$$

Similarly as before, ξ_2 includes both the Förster ET contribution, ϕ''_{Fs}, and the reabsorption Θ''. γ is defined as:

$$\gamma = \int I_E\varepsilon_{SS}d\lambda \quad , \qquad \text{(Eq. S10)}$$

where I_E is the normalized emitter fluorescence and ε_{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^2_{cs}) at the second step:

$$N^2 = (N_{TT}\xi_2)\xi_1, \qquad \text{(Eq. S11)}$$

$$N^2_{cs} = \frac{1}{2}N^2 f\phi_{TTA}(1 - \phi''_{Fs})\phi_E = N^2 \times QY_{uc} \times (1 - \phi''_{Fs}). \qquad \text{(Eq. S12)}$$

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

$$N^{(i)} = N^1 \left\{ \frac{1}{2} f \phi_{TT} \xi_1 \xi_2 \right\}^i, \qquad \text{(Eq. S13)}$$

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

$$N_{cs} = \sum_{i=0}^{n} N^{(i)} \frac{1}{2} f \phi_{TTA} \left(1 - \phi_{Fs}^{''}\right) \phi_E = \sum_{i=0}^{n} N^{(i)} \times QY_{UC} \times \left(1 - \phi_{Fs}^{''}\right). \qquad \text{(Eq. S14)}$$

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

$$N_{cs} = N_0 \times QY_{uc} \times \left(1 - \phi_{Fs}^{''}\right) \times \left(1 + \Omega \xi_1\right) \times \left(1 - \frac{QY_{uc}}{\phi_E} \xi_1 \xi_2\right)^{-1}, \qquad \text{(Eq. S15)}$$

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 η:

$$\eta = \left(1 - \phi_{Fs}^{''}\right) \times \left(1 + \Omega \xi_1\right) \times \left(1 - \frac{QY_{uc}}{\phi_E} \xi_1 \xi_2\right)^{-1}. \qquad \text{(Eq. S16)}$$

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:

$$QY_x = QY_{std}\left(\frac{A_{std}}{A_x}\right)\left(\frac{I_x}{I_{std}}\right)\left(\frac{n_{std}}{n_x}\right)^2, \qquad \text{(Eq. S17)}$$

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 3×10^{-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%.

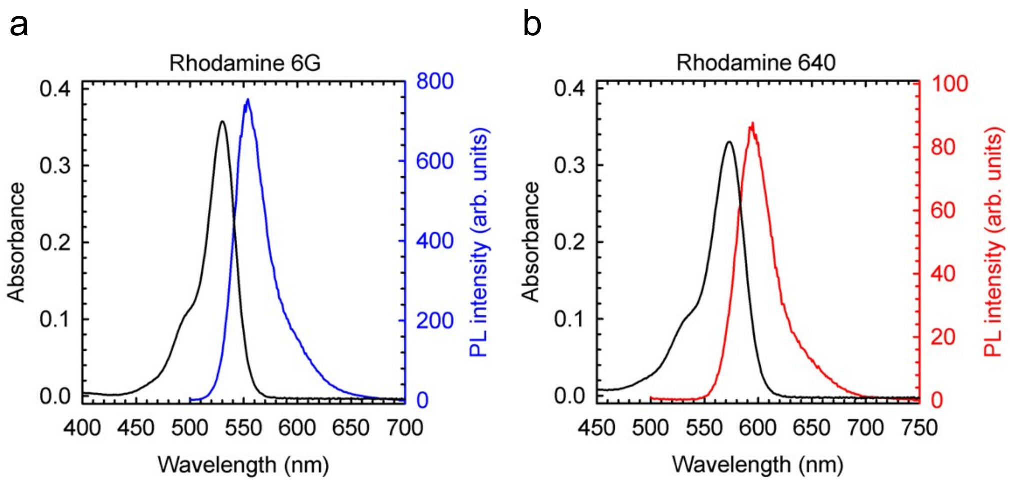

Fig. S2 Absorption (black line) and Photoluminescence spectra (blue, red lines) for (a) Rhodamine 6G 3×10^{-5} M in EtOH and (b) Rhodamine 640 10^{-4} M in THF:MeOH 2:1, respectively.

We used Eq. S17 to estimate the *cs*TTA-UC QY. The addition of the Rh640 in the optimal concentration (5×10^{-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 (~10^{17} photons cm^{-2} s^{-1}). By considering that the number of emitted photons in *cs*TTA-UC in this conditions increases of a factor ~1.2 respect to the reference TTA-UC, and using the n values reported in (Parveen 2009), Eq. S17 becomes

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

The standard *s*TTA-UC system taken as reference for this experiment is composed of $PdPh_4TBP$ (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 concertation < 0.1 ppm.

4. Calculation and Measurements of Förster ET efficiencies

The relation for η shown in Eq. S16 is critically dependent on the energy transfer efficiencies between the three chromophores composing the *cs*TTA-UC system. As said before, for the optimized TTA-UC system composed of $PdPh_4TBP$ and perylene we have ϕ_{Dx}=100%. However, ϕ'_{Fs} and ϕ''_{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:

$$\phi_{ET}(C_A) = \frac{k_{DA}(C_A)}{k_{D,0} + k_{DA}(C_A)} \qquad \text{(Eq. S19)}$$

$$= 1 - \frac{I_D(C_A)}{I_{D,0}}, \qquad \text{(Eq. S20)}$$

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 $PdPh_4TBP$ (from 10^{-8} M to 10^{-3} M) compared with a Rh640 sample with no $PdPh_4TBP$ (Fig. S3). Fig. S3 shows that for our system the Fs' efficiency is 45%.

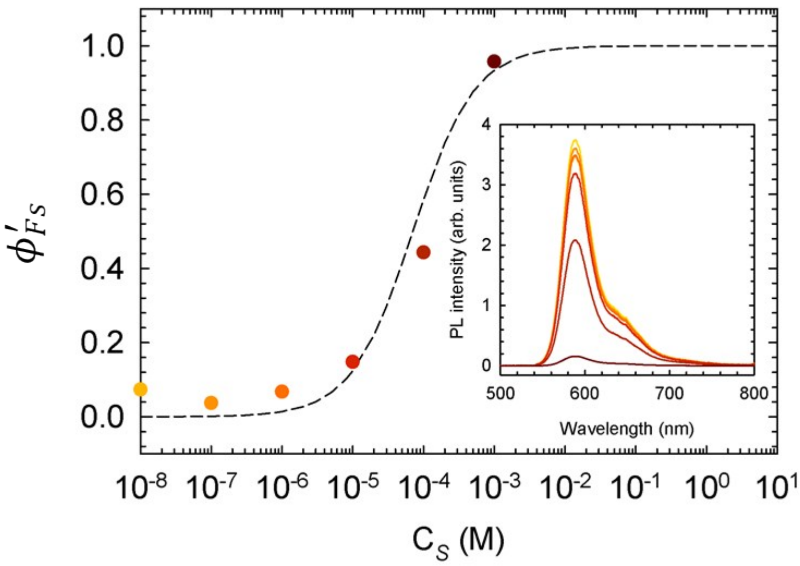

Fig. S3 Fs' efficiency as a function of the *S* concentration. The coloured dots show the experimental values as calculated with Eq. S20 from C_S=10^{-8} M (yellow dot) to C_S=10^{-3} M (dark red dot). The black dashed line shows the ET values predicted by Eq. S22. The inset shows the *SS* PL intensity measured with increasing *S* concentration (from C_S=10^{-8} M to C_S=10^{-3} M) and without sensitizer.

To calculate the Fs'' 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).

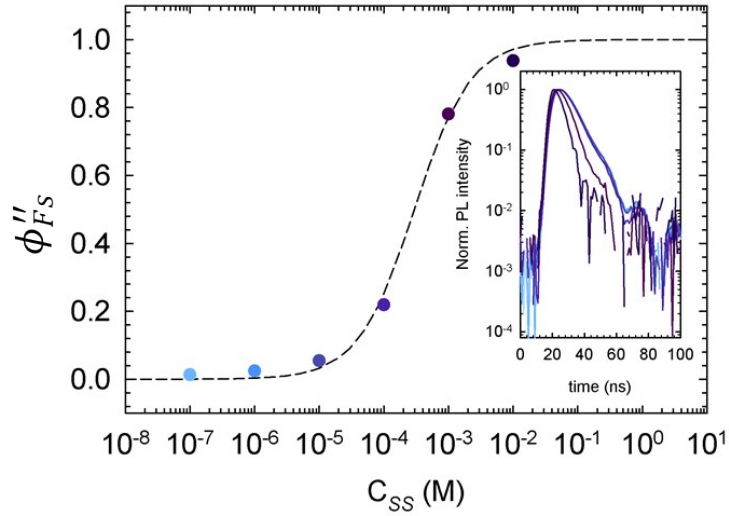

Fig. S4 Fs'' efficiency as a function of the *SS* concentration. The coloured dots show the experimental values as calculated with Eq. S20 from C_{SS}=10^{-7} M (bright blue dot) to C_{SS}=10^{-2} M (dark blue dot). The black dashed line shows the ET values predicted by Eq. S22. The inset shows the emitter 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 Fs'' rate k_{DA} has been calculated for the given concentration, we estimated the Förster radius R_0 from the relation:

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

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 Fs'' efficiency as a function of C_{SS}:

$$\phi_{Fs}^{'} = \frac{\frac{4}{3}\pi R_0^6 a^{-3} \rho_A}{1 + \frac{4}{3}\pi R_0^6 a^{-3} \rho_A} . \qquad \text{(Eq. S22)}$$

From Eq. S22 it is possible to calculate the Fs'' efficiency for any C_{SS}.