**ELECTRONIC SUPPLEMENTARY INFORMATIONS**

# Achieving the Photon Up-conversion Thermodynamic Yield Upper Limit by Sensitized Triplet-triplet Annihilation.

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## 1. Self-absorption and re-absorption PL Correction

QY measurements on sTTA-UP systems made on concentrated solutions may be affected by both self-absorption (i. e. absorption of the up-converted emission by the emitter itself) and re-absorption (i. e. absorption of the up-converted emission by the sensitizer). The first effect is particularly relevant when the emitter absorption-emission Stokes-Shift is small, while the second one becomes important when there is a non-negligible overlap between the photoluminescence spectrum of the emitter and the absorption spectrum of the sensitizer. Both these problems can be addressed using one of the spectral-based method reported in the literature [J. C. De Mello et al., Adv. Mater., 9, 230 (1997); L. O: Palsson et al., Adv. Mater., 14, 757 (2002); Thi-Sanh Han et al., Rev. Sci. Instrum., 78, 086105 (2007)] and are have been considered in the investigated $PdPh_4TBP$/PY sTTa-UP system.

a) Self-absorption.

Self-absorption is evident in concentrated PY solutions whose photoluminescence spectra show a progressive reduction of the first emission peak at 2.81 eV up to its completely disappearance for a PY concentration of $10^{-3}$ (Fig. S1). Following the above mentioned reference, the real QY can be calculated from QY measured experimentally ($QY_{exp}$) as

$$\mathrm{QY} = \frac{\mathrm{QY}_{exp}}{1 - a + a\mathrm{QY}_{exp}}, \qquad \text{Eq. S1}$$

in which $a$ represent the fraction of re-absorbed photons. $a$ is evaluated from the photoluminescence spectra collected on diluted solution ($PL'_{exp}$) and on the investigated sample ($PL_{exp}$)

$$1 - a = \frac{\int \mathrm{PL}_{\exp}(\lambda)\mathrm{d}\lambda}{\int \mathrm{PL}'_{\exp}(\lambda)\mathrm{d}\lambda} . \quad \text{Eq. S2}$$

If we use the PY solution at $10^{-6}$ M as reference, the $\phi_{fl}$ for the samples at $10^{-3}$ M and $10^{-4}$ M raises from the value reported in Tab. 1 to 0.76 and to 0.85 respectively, while the $\phi_{fl}$ for the sample at $10^{-5}$ M does not change significantly. However, the lack in efficiency is not completely cancelled by self-absorption correction. This is because perylene photoluminescence concentration quenching is given by excimers formation as clearly demonstrate in the literature (see Ref. 25, 26 in the main text). Because it is not possible to avoid excimers formation, the fluorescence concentration quenching is the limiting factor of sTTA-UC yield in systems exploiting perylene as annihilator and emitter.

In our experiment, we note that, because exactly the same corrections must be applied also to $\mathrm{QY}_{out}$, the values of the statistical parameter $f$ calculated with the Eq. 1, and reported in Tab. 1, do not change.

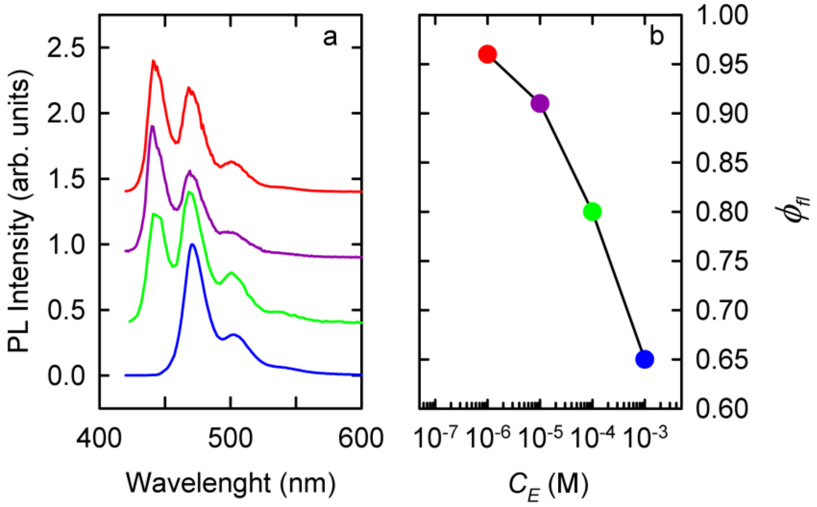

**Figure S1.** (a) PY normalized photoluminescence spectra (excitation 380 nm) at different concentration $C_E$ in THF and (b) corresponding measured fluorescence quantum yield $\phi_{fl}$.

Fig. S2 depicts the normalized absorption spectrum of PY solution in THF at the lowest ($10^{-6}$ M) and higher ($10^{-3}$ M) used in the experiment. None signficant change is detectable, thus we exclude that PY fluorescence quanching is significantly determined by the formation of stable aggregates between dyes in solution.

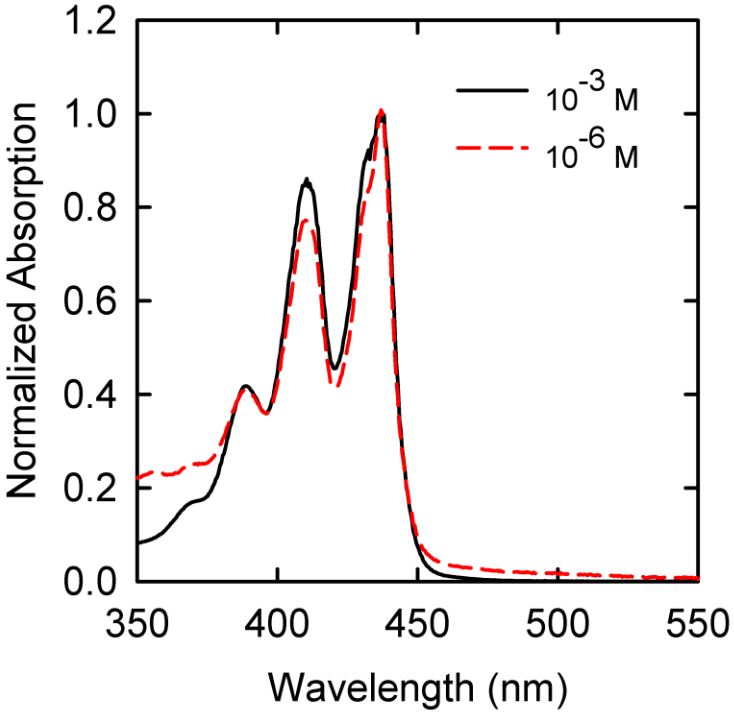

**Figure S2.** (a) PY normalized absorption spectra in THF solution (solid line $10^{-3}$ M and dashed line $10^{-6}$ M).

b) Re-absorption.

The QY correction for the re-absorption cannot be done directly with the above reported equations since the re-absorbed photons experiment all the photophysical sTTA-UP steps before producing a PY emitting singlet. In our systems this effect is in general small (the concentration of $PdPh_4TBP$ is only $10^{-5}$ M), and affects mainly the data of the samples at low PY concentrations in which the origin of the PL vibronic progression largely overlap the *B*-band of the $PdPh_4TBP$ absorption spectrum. However, this are: i) the samples with the lowest sTTA-UP efficiencies, and ii) the samples for which the *f* evaluation is not reliable. For these reasons, we neglect this correction.

## 2. Energy Transfer Measurements vs $C_E$

The ET yield has been calculated as $\phi_{ET} = 1 - I/I_0$, where $I_0$ is the intensity of the sensitizer photoluminescence in absence of emitters under 1.95 eV continuous wave excitation (black line in the inset of Fig. S3) and $I$ is the intensity of the same emission for the given emitter concentration $C_E$.

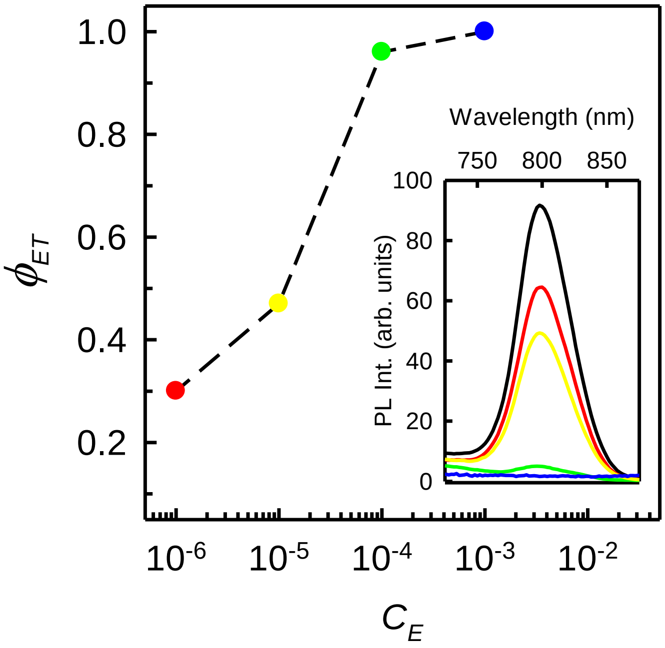

**Figure S3**. ET efficiency $\phi_{ET}$ as a function of the PY concentration $C_E$. The inset shows the recorded PL spectra as a function of the acceptor concentration (the black line was recorded without the acceptor).

## 3. Relative Up-conversion Quantum Yield Measurements

$QY_{out}$ and PY $\phi_{fl}$ has been determined by relative photoluminescence intensity measurements by using phthalocyanine in 1-chloronaphthalene as a standard. The following formula has been used for the calculation of the unknown yield

$$\Phi_{unk}=\Phi_{unk}\left(\frac{I_{std}}{I_{unk}}\right)\left(\frac{A_{std}}{A_{unk}}\right)\left(\frac{E_{unk}}{E_{std}}\right)\left(\frac{\eta_{unk}}{\eta_{std}}\right)^2 \qquad \text{Eq. S3}$$

where $\Phi$, $I$, $A$, $E$, and $\eta$ represent the quantum yield, excitation intensity, absorptance, integrated photoluminescence spectral profile, and refractive index of the solvent. The subscripts *unk* and *std* denote the parameters relative to the unknown and standard systems. Photoluminescence signals were recorded by a nitrogen cooled CCD coupled with a spectrograph Triax-190 (Horiba Jobin-Yvon), with a spectral resolution of 15 nm. The slit width was 0.5 mm, much larger than the image of the excitation laser-spot diameter in order to avoid incorrect signal detection of photoluminescence due to the different position of the focal plane at different wavelengths. Excitation laser stray-light has been removed by a proper notch filter. the PL spectra have been also carefully corrected for the system optical response.