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

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Triplet-triplet annihilation (TTA) based up-conversion is a promising strategy for light harvesting the low-energy tail of the solar spectrum in photovoltaic technologies. Here we present a bi-component system for photon managing via TTA that allows bypassing the classical statistic limit of 2/5 in the singlet generation, achieving a nearly unitary conversion efficiency. This result is obtained thanks to the peculiar relative position of the triplet and singlet energy levels of perylene, used as up-converter and emitter. The system shows under an irradiance of 1 sun, a record red-to-blue external up-conversion yield of ~10%.

Solar technologies are the most common and sustainable strategies for the production of carbon-free renewable energy with a significant impact for long-term worldwide growth. However, the efficiency of photovoltaic and photo-catalytic devices for hydrogen production is limited because they exploit only a fraction of the available light.[1-5] To use efficiently also the low-energy tail of the solar spectrum an improved light harvesting can be achieved by up-conversion (UC) of sub-bandgap photons through different processes that must be effective in the light managing at the solar irradiance. At the present, this requirement can be fulfilled only by the so-called sensitized triplet-triplet annihilation (sTTA-UC) in multi-component organic systems. Briefly, an up-converting molecule, the acceptor/emitter, gives rise to high-energy delayed fluorescence upon annihilation of its metastable triplet states, which are populated trough Dexter energy transfer (ET) from the triplet states of a proper light harvester, the donor/sensitizer. In this latter the triplet states are generated *via* intersystem crossing (ISC) from singlet states excited upon low-energy light absorption.[6] After a very fast development, different groups reported sTTA-UC systems with up-conversion yields as high as 20% under an irradiance of few *suns*. These performances are order of magnitude better than those achievable with up-converters based on other processes, as multi-photon absorption or annihilation of rare-earth excited states.[7-10] Because sTTA-UC materials were also proven to effectively enhance the light-harvesting efficiency of real PV devices, [3, 5, 11, 12] it is candidate to become a fundamental building block for the next generation of solar-based devices, with a potential yield enhancement as high as 50% for silicon and organic photovoltaic cells, and even larger for photo-catalytic water splitting cells (+100%).[8, 13, 14]

The maximum quantum-yield (QY) of the photon UC is 0.5 because, obeying to the thermodynamic requirement $2E_{in} \geq E_{out}$, two low-energy (E_{in}) photons are required to generate one photon with higher energy (E_{out}). However, in the case of the sTTA-UC, the intrinsic probability that emitting states are effectively generated upon TTA introduces an additional statistic requirement, which decreases the limit QY from 0.5 to 0.2 (see below). Here we describe for the first time an up-converting system in which the statistic limit is bypassed obtaining an internal UC efficiency QY_{int} ~0.5. The external sTTA-UC quantum yield (QY_{out}) is 0.38, limited only by the efficiencies of the sensitizer-emitter ET and of the emitter fluorescence at the employed concentration.

The sTTA-UC yield depends on the product of the efficiencies of all the involved photophysical steps

$$\mathrm{QY}_{out} = 0.5 f \phi_{ISC}\phi_{ET}\phi_{TTA}\phi_{fl} = \phi_{ISC}\phi_{ET}\phi_{fl}\mathrm{QY}_{int}, \qquad \text{Eq. 1}$$

where the pre-factor 0.5 is set by the thermodynamic limit described above. The other parameters are the efficiencies of the sensitizer ISC (ϕ_{ISC}), the sensitizer-emitter energy transfer (ϕ_{ET}), the emitter TTA (ϕ_{TTA}) and fluorescence (ϕ_{fl}). In Eq. 1, f represents the probability to obtain a singlet excited state as a result of the annihilation of two triplet states.[15] Cheng and co-authors recently introduced a discussion on this parameter. It depends on the electronic properties of the systems that experience bi-molecular excitonic annihilation, and they suggested how it is possible to overcome the spin statistical limit for TTA assisted up-conversion yield. [11, 16]

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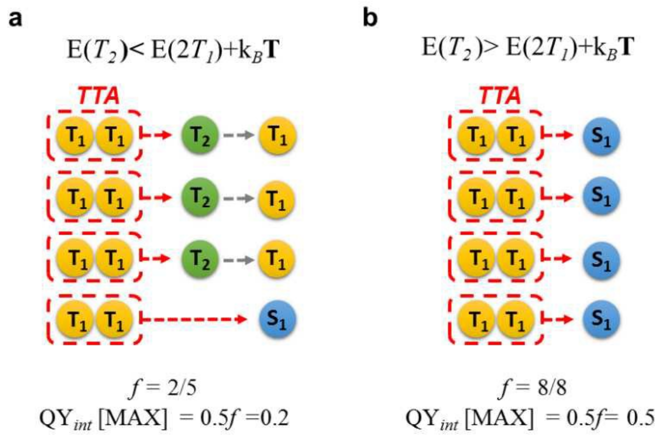

Fig. 1 Sketch of the TTA process involving four triplet pairs. In the case (a), where T_2 levels are energetically accessible, the collision of four triplet pairs destroy five triplets. Only two dead triplet produce a singlet excited state, therefore f = 2/5 = 0.4 with a predicted maximum QY$_{int}$= 0.2 (Eq. 1). In case (b), where the T_2 level is not energetically accessible, the collision of four triplet pairs produces four singlet excited states. Thus f = 8/8 = 1, with a predicted maximum QY$_{int}$ = 0.5.

Indeed, TTA is a two-particle collision process, which results in the generation of excitons with different spin-character according to the statistical combination of the spin of the colliding triplets. TTA reactions are described as

$$T_1 + T_1 \rightleftarrows \langle T_1 \cdots T_1 \rangle \Rightarrow \begin{cases} Q + S_0 \text{ (multiplicity 5)} \\ T_2 + S_0 \text{ (multiplicity 3)} \\ S_1 + S_0 \text{ (multiplicity 1)} \end{cases} . \qquad \text{Eq. 2}$$

Quintet (Q) states require the simultaneous excitation of two electrons and are energetically unattainable. On the contrary, usually E(T_2)<E(2T_1)+k$_B$**T** and E(S_1)<E(2T_1)+k$_B$**T** allowing the intermediate collision complex to generate either a singlet excited state S_1 or one of the tree degenerate high-energy T_2 triplet states with a statistical ratio of 1:3. The resulting T_2 states quickly decay back to T_1, becoming again available for further annihilations (see Fig. 1a). Therefore, upon collision of four triplet exciton pairs five triplets are destroyed, but only two of them give a singlet, which sets f=2/5. However, if E(T_2)>E(2T_1)+k$_B$**T**, not only the formation of quintet state is prevented, but also that of high-energy triplets. In this case, only singlet excitons can be formed upon TTA, thus f =1 (see Fig. 1b). This latter is the fundamental requirement to bypass the statistic limit and to reach a maximum QY$_{int}$ =0.5.[11, 16]

The emitters commonly used in the sTTA-UC are rigid polyacenes. They possess a large fluorescence yield (ϕ_{fl} ~1) and long-living metastable triplets suitable for TTA. As sensitizers, metallated porphyrins show the best performance. They have a strong absorption cross-section thanks to the conjugated porphyrinic ring, and fast ISC enhanced by the presence of the central metal atom which gives ϕ_{ISC}=1.[17, 18] Therefore, by using properly paired chromophores of these families we can avoid energy losses by unwanted non-radiative processes. Of course, the lowest excited state of the sensitizer must be resonant with the T_1 level of the emitter in order to allow the Dexter ET. If this requirement is satisfied, ϕ_{ET} can be easily optimized by changing the emitter concentration (C_E). In order to demonstrate the possibility to overcome the sTTA-UC statistic limit, as emitter we selected in the polyacene family the *perylene* (PY).[19, 20] PY is the ideal molecule for this purpose, as its ϕ_{fl} is 0.96 in diluted solution, the $T_1 \leftrightarrow S_0$ transition is strictly forbidden implying a T_1 natural lifetime in the range of 5 ms, and, in particular, E(T_2) ~4.0 eV is much larger than twice E(T_1) ~1.51 eV.[21-23] As concern the sensitizer we choose the palladium(II) *meso-tetraphenyltetrabenzoporphyne* (PdPh$_4$TBP), a near-infrared emitting phosphor with ϕ_{ISC}=1 and a strong phosphorescence at 1.56 eV, not far from the T_1 state of PY. Moreover, the broad PY photoluminescence ranging from about 2.40 and 2.80 eV falls mainly in the transparency window of PdPh$_4$TBP delimited by the β- and the Q- absorption bands at 2.81 and 1.96 eV. Very similar systems has been previously employed by Singh-Rachford and Castellano to achieve red-to-blue sTTA-UC achieving good results for the conversion yield.[24]

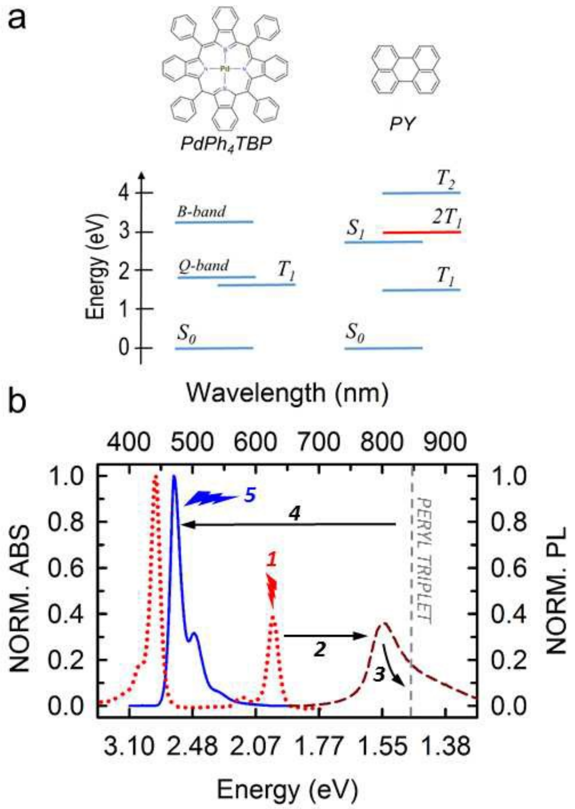

Fig. 2 (a) PdPh$_4$TBP molecular structure and energy levels. (b) Absorption/emission of PdPh$_4$TBP (dotted red and dashed brown lines, respectively) and up-converted photoluminescence of PY (solid blue line). Numbered arrows indicate the sTTA-UC relevant photophysical steps: 1) low-energy absorption, 2) ISC, 3) sensitizer-emitter Dexter Energy transfer, 4) TTA, 5) high energy emission.

The spectroscopy study was performed by dissolving both the dyes in tetrahydrofuran (THF) with a fixed concentration of PdPh$_4$TBP (10^{-5} M) and a changing that of PY from 10^{-3} M to 10^{-6} M. Absorption measurements were done with a Cary 50 spectrometer. 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. As

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excitation source a Roithner solid-state laser diode RLTMRL-635-100-5 at 1.95 eV (635 nm) was generally used. Only for the photoluminescence QY measurements this laser was replaced with the second the harmonic of a Ti:Sapphire laser at 3.26 eV (380 nm). QY_{out} and PY ϕ_{fl} has been determined by relative photoluminescence intensity measurements by using phthalocyanine in 1-chloronaphthalene as a standard (see ESI for details).[21] All samples were prepared by using anhydrous solvents, and were sealed in a glove box in quartz cuvettes with an optical path d=0.1 cm to prevent oxygen quenching. Chemicals were received from Sigma Aldrich and used as is.

Fig. 2 reports the molecular structure with the relevant energy levels of the employed chromophores (upper panel), and the absorption/emission spectra of PY and $PdPh_4TBP$ (lower panel). Numbered arrows outline the energy flow in the sTTA-UC process. The sensitizer absorbs light at E_{in}=1.95 eV (**1**) and then experience a fast ISC that populates its triplet state at 1.55 eV (**2**). PY triplets are excited by Dexter energy transfer from donors (**3**) and experience TTA (**4**), thus generating fluorescent singlets at E_{out} =2.61 eV (**5**). The overall photon-energy gain is $\Delta E=(E_{out}- E_{in})$=0.66 eV. In the case of samples at low PY concentration, the photophysics remains the same, but the up-converted emission slightly shifts to higher energy as described in the Electronic Supplementary Information (ESI) file. Fig. 3 reports the measured QY_{out} plotted vs the excitation power density (I_{exc}) in a log-log scale for samples with different C_E. The QY_{out} data have been corrected nor for the PY self-absorption neither for the $PdPh_4TBP$ re-absorption. These two effects play a minor role in determining the performances of the systems and are discussed in the detail in the ESI. Here we outline that this is a quite conservative approach, as the inclusion of the above-mentioned effects results in performances even better than the reported ones. For all the samples at low excitation power, QY_{out} is below 1%, as the density of PY triplet states is too low to have any efficient annihilation being the spontaneous non-radiative decay the main triplet de-excitation channel. By rising the exciting radiant flux, we observe a corresponding QY_{out} increase up to a constant value. This is reached when the TTA becomes the dominant deactivation channel for the metastable triplets.[22] In some cases, i. e. samples with C_E $=10^{-5}$ M and in particular $C_E=10^{-6}$ M, the regime in which QY_{out} is excitation power-independent is followed by a strong decrease of the conversion yield. This is due to the saturation of the number of acceptors available for the ET occurring when I_{exc} is so large that a not-negligible fraction of the emitters is in an excited state.[25]

We firstly studied the sample with $C_E=10^{-3}$ M, the maximum concentration of emitter soluble in THF (Fig. 3, circles). The regime in which the conversion yield assumes a constant value is reached for I_{exc} $>10^{16}$ph cm^{-2} s^{-1}. Here, we measure QY_{out}=0.33. The singlet generation efficiency upon TTA can be now evaluated from Eq. 1 by considering that: i) donor ϕ_{ISC} is 1, because in the $PdPh_4TBP$ there is no detectable fluorescence from the absorbing S_1 state.[26] ii) ϕ_{TTA} is 1, as we are considering the irradiance range in which QY_{out} is independent from I_{exc}, i. e. in which all the triplet states decay by annihilation. iii) Thanks to the large C_E concentration, ϕ_{ET} =1 as demonstrated by ET efficiency measurements (ESI, Fig. S2). iv) The ϕ_{fl} of PY at this concentration is only 0.65 because of the concentration quenching effect at the selected C_E (see ESI, Fig. S1).[27, 28] As a matter of fact, PY fluorescence efficiency is the only the bottleneck for the conversion yield in the investigated system. With these values, Eq. 1 gives $QY_{int}=QY_{out}(\phi_{ET}\phi_{fl})^{-1}$ =0.49, or equivalently f=1. This demonstrates for the first time that the thermodynamic upper limit of photon up-conversion yield by TTA is reached. The overall sTTA-UC efficiency can be increased optimizing the system composition by decreasing the emitter concentration down to $C_E=10^{-4}$ M, in order to limit the concentration quenching of ϕ_{fl} (Fig. 3, dots). In such a way, ϕ_{fl} = 0.80, and C_E is still high enough to get ϕ_{ET}=0.97 (ESI, Fig. S1). The measured QY_{out}=0.38 is, to our knowledge, the highest value observed for photon sTTA-UC. Again by Eq. 1, the calculated QY_{int}=0.50 confirms an f value of 1. Additional reductions of C_E allow to further reduce the emitter fluorescence quenching, but limit the ET efficiency and, as a consequence of the described saturation effect, hamper the correct evaluation of f. In the system with $C_E=10^{-5}$ M, from one side ϕ_{fl} rises up to 0.91±0.04 but from the other one the corresponding ϕ_{ET} decreases down to 0.47 and the maximum measured sTTA-UC efficiency to 0.19. In this case, Eq. 1 gives QY_{in}=0.42 at which corresponds f=0.8. This suggests that the ET saturation at high excitation intensities prevents reaching the maximum achievable QY_{out} giving a unreliable value of f. This is confirmed by the data collected for the sample with the smallest C_E = 10^{-6} M that shows a dramatic decrease of QY_{out} well before its saturation value is reached. Table 1 summarizes the relevant parameters for all the investigate samples measured at I_{exc}= $8x10^{17}$ ph cm^{-2} s^{-1} (250 mW cm^{-2}). In the inset of Fig. 3 a picture of the bright blue emission of the sample $PdPh_4TBP$/PY (10^{-5} M/10^{-4} M) excited with a white lamp passing through a 520 nm long-pass optical filter demonstrates the high efficiency of the sTTA-UC in our system. For this sample it should be outlined that, even if it is necessary an

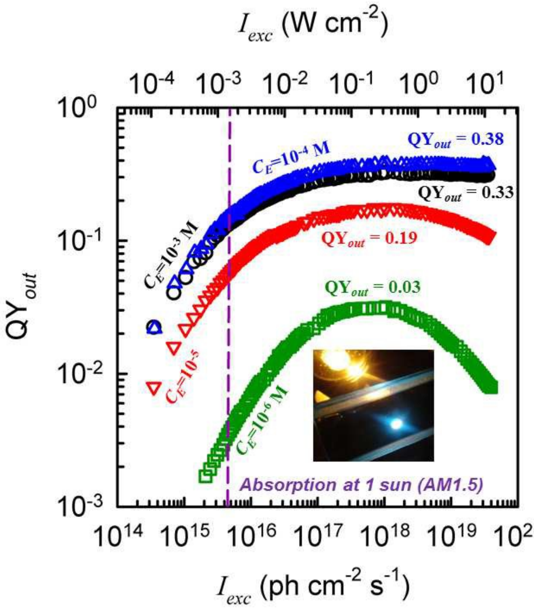

Fig. 3 sTTA-UC quantum yield at 2.61 eV under CW excitation at 1.95 eV for a THF solution of $PdPh_4TBP$ 10^{-5} M and PY 10^{-3} M (dots), 10^{-4} M (circles) 10^{-5} M (triangles), and 10^{-6} M(squares) as a function of the excitation intensity I_{exc}. The inset show the sTTA-UC emission of a THF solution (10^{-5} M/ 10^{-4}M) under broad excitation by a filtered white lamp. The dashed vertical line indicates the amount photons absorbed under 1 sun of irradiance by considering the sensitizer absorption at the concentration of 10^{-5} M used in the experiment.

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Table 1. Main efficiencies measured/calculated for the investigated samples (I_{exc}= 8x10^{17} ph cm^{-2} s^{-1}). * indicates that the corresponding value may be underestimated because of an ET saturation effect.

$PdPh_4TBP/PY$ Conc. (M)	ϕ_{ET}	ϕ_{fl}	QY_{out}	QY_{int}	f
$10^{-5} : 10^{-3}$	1.00 ±0.05	0.65 ±0.03	0.33 ±0.02	0.49 ±0.07	1.0 ±0.1
$10^{-5} : 10^{-4}$	0.96 ±0.05	0.80 ±0.04	0.38 ±0.03	0.50 ±0.07	1.0 ±0.1
$10^{-5} : 10^{-5}$	0.47 ±0.02	0.91 ±0.04	0.18 ±0.01	0.42 ±0.06*	0.8 ±0.1*
$10^{-5} : 10^{-6}$	0.03 ±0.01	0.95 ±0.05	0.03 ±0.01	-	-

excitation power density larger than the solar irradiance to obtain its maximum efficiency, the QY_{out} achievable by absorbing a number of photons equal to that provided by the solar irradiance at the A.M. 1.5 condition(Fig. 3 dashed vertical line) is as large as ~10%.

Conclusions

In conclusion, the thermodynamic upper limit of ~50% in photon up-conversion yield has been demonstrated for a sTTA-UC system by using an acceptor/emitter dye pair with suitable triplet and singlet energy levels. When the condition $E(S_1)<E(2T_1)+k_B\mathbf{T}<E(T_2)$ is satisfied, the singlet generation by TTA is maximized, and the QY_{out} is only limited by the emitter fluorescence efficiency, and/or by the sensitizer-to-emitter energy transfer yield. Our findings demonstrate that by a proper selection of the chromophores it is possible to have up-conversion yields not only at low irradiance,[20, 29, 30] but also without photon losses exactly as in the case of non-linear optic materials when they operate with coherent radiation at excitation power densities of MW or GW per square centimetre. Thanks to his record performance, the sTTA-UC system presented show an up-conversion efficiency of 10% under 1 sun of irradiance, demonstrating the potential application of these materials in photovoltaic and photo-catalytic technologies.

Notes and references

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Electronic Supplementary Information (ESI) available: Details and discussions on the photoluminescence quantum yield and energy transfer yield measurements. See DOI: 10.1039/c000000x/

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