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Triplet-Triplet Annihilation Photon-Upconversion: Towards Solar Energy Applications†

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Solar Power Production and Solar Energy Storage are important research areas for development of technologies that can facilitate a transition to a future society independent of fossil fuel based energy sources. Devices for direct conversion of solar photons, suffer from poor efficiencies due to spectrum losses, which are caused by energy mismatch between the optical absorption of the devices and the broadband irradiation provided by the sun. In this context, photon upconversion technologies are becoming increasingly interesting since they might offer an efficient way of converting low energy solar energy photons into higher energy photons, ideal for solar power production and solar energy storage. This perspective discusses recent progress in Triplet-Triplet Annihilation (TTA) photon upconversion systems and devices for solar energy applications. Further, challenges with evaluation of the efficiency of TTA-photon upconversion systems are discussed and a general approach for evaluation and comparison of existing systems is suggested.

Introduction

Arguably, the only solution that can sustainably satisfy society's ever-growing demand for energy, is to capture sunlight and convert it into useful and storable forms of energy.[1] Many different approaches are currently under investigation including solar electricity generation using various kinds of solar cells and solar fuels generation.[2–9] The majority of devices for direct conversion of solar photons, suffer from poor efficiencies due to the so-called spectrum losses. The origin of these losses is twofold: Firstly, the photon conversion processes typically require photon energies above a certain threshold to occur. Secondly, surplus energy from photons with energy above this threshold-value is wasted. Thus, for radiation at the blue end of the spectrum, only a fraction of the photon energy is captured and the rest dissipated as heat. At the red end of the solar spectrum, radiation with too long wavelengths is not able to contribute to fuel or electricity production.

Considering the lower photon energies, one way to make better use of the solar irradiation would be photon upconversion, meaning that two low-energy photons are used to produce one photon with higher energy. For any real-world application, this process must work using diffuse sunlight and therefore mainly two kinds of upconversion systems are considered, namely those based on rare earth metals and those based on sensitized Triplet-Triplet Annihilation (TTA) of organic molecules[10]. In this perspective the TTA process is the primary focus. Parker and Hatchard reported the first example of this already in 1962.[11] The TTA photon upconversion process involves a sensitizer molecule (S) which is excited to its first singlet excited state ($^1S \rightarrow ^1S^*$), subsequently the sensitizer undergoes efficient intersystem crossing (ISC) forming its corresponding triplet species ($^3S^*$). The triplet excited sensitizer transfers its energy to an annihilator (sometimes referred to as "emitter") molecule (A) through Triplet Energy Transfer (TET), forming a triplet annihilator species ($^3A^*$). In the final steps of the process two $^3A^*$ molecules combine through TTA forming one annihilator in its ground state (^1A) and one singlet excited annihilator ($^1A^*$), which in turn can emit a photon when relaxing to its ground state (a further description is summarized in ESI).

While the progress was slow to begin with, the development of metallated triplet sensitizers and later metal-free triplet sensitizers[12-14] has caused a renewed interest in the field, and several reviews have been published in recent years.[15-20] In this perspective, our focus is directed toward solar energy demonstration devices. Furthermore, we discuss the experimental methodologies used to evaluate TTA systems and discuss the need for a more standardized method to evaluate these systems, a method that takes into account factors such as excitation light intensity and wavelength and intensity distribution.

How to evaluate Triplet-Triplet Annihilation photon-upconversion (TTA-UC) systems

Upconversion quantum efficiencies for various upconversion fluorophore pairs are being readily reported; however there exists no widely accepted standardized way to calculate such efficiencies today. This makes it difficult to compare different upconversion systems directly in a fair and consistent way. Some of the reasons behind this are the strong dependency on the relative sensitizer/annihilator concentrations as well as the quadratic dependency on excitation power. Generally, the quantum yield of photon upconversion through TTA can be defined as[16]

$$\Phi_{\mathrm{UC}} = \Phi_{\mathrm{S.ISC}}\Phi_{\mathrm{TET}}\Phi_{\mathrm{TTA}}\Phi_{\mathrm{A.F}} \qquad (1)$$

where $\Phi_{S,isc}$ is the quantum yield of intersystem crossing (*ISC*) of the sensitizer, Φ_{TET} is the quantum efficiency of the Triplet Energy Transfer (TET) from the sensitizer in its triplet excited state ($^3S^*$) to the annihilator in its singlet ground state (^1A):

$$\Phi_{TET} = \frac{k_{TET}[^1A]}{k_{TET}[^1A]+2k_{TTAS}[^3S^*]+k_{PS}} \qquad (2)$$

Here, k_{TET} is the TET rate constant, k_{TTAS} is the TTA rate constant for the triplet sensitizer and k_{PS} is a sum of all radiative and non-radiative first- and pseudo-first order rates for deactivation of the sensitizer triplet state. Φ_{TTA} is the quantum efficiency of the TTA between two annihilators in their triplet excited states ($^3A^*$),

$$\Phi_{TTA} = \frac{k_{TTA}[^3A^*]}{2k_{TTA}[^3A^*]+k_{PA}} \qquad (3)$$

where k_{TTA} is the TTA rate constant for the triplet excited annihilator, ($^3A^*$), and k_{PA} is the same sum of deactivation processes as k_{PS} in eq. (2) but instead for the triplet excited annihilator. Finally, $\Phi_{A,f}$ is the fluorescence quantum yield of the annihilator. Please, refer to the Supplementary information (ESI)[†] for a derivation of equations (2) and (3).

In the low excitation intensity region, the first- and pseudo-first order mechanisms of the triplet species deactivation (k_{PS}, k_{PA}) dominate, causing the overall upconversion process to function at quantum efficiency that is below its maximum. Experimentally this results in a quadratic intensity dependence of the upconversion emission intensity on the excitation power density.[21-27] Once the excitation intensities increase to and beyond the point where the TET- and TTA-processes eq. (2) and (3) dominate the deactivation of the triplet species, the upconversion quantum efficiency reaches a stationary level. This results in a linear intensity dependence of the upconversion emission on the excitation power, as observed experimentally.[22-31] Based on equations (1-3) the absolute maximum upconversion quantum yield obtainable at sufficiently high excitation intensity would be 50% due to the factor of 2 in the denominator of equation 3. The factor 2 originates from the stoichiometry of the TTA process where two triplet excited annihilators are required to generate one singlet excited annihilator. However, as can be seen in eq. (2), high excitation intensities or high triplet sensitizer concentrations can reflect negatively on the TET-quantum efficiency due to self-annihilation[32] of the triplet sensitizers. This negative contribution is rarely seen for "normal" excitation conditions in experiments done in fluid solution where sensitizer concentration is low but could be a quite substantial effect in polymeric systems where sensitizer concentrations typically are much higher. It can, however, be minimized through composition optimization of the sensitizer and annihilator.

It has been argued that the theoretical limit of the TTA process cannot exceed the spin statistical limit of 1/18 (5.55 %)[¶], which in turn also limits the overall upconversion efficiency. The reason for this limit is the preservation of spin multiplicity of the two annihilating triplets. Spin-statistics predict that a TTA-event results in 9 possible scenarios – 3×3 combinations of electron spin multiplicities – where 5 would yield quintet, 3 would yield triplet and 1 would yield singlet excited state multiplicity of the initial encounter complex.[33] However, one must also consider the progression of such complexes where the quintets would normally be forced to relax back to the two initial triplets since a quintet excited state of one annihilator molecule would normally require higher energies than available from the sum of two triplet energies. The triplet encounter complex would result in a higher excited triplet annihilator carrying two triplet quanta that could internally convert to one of the initial triplet annihilators carrying one triplet quanta.[34,35]

Considering this argument, the theoretical limit of the TTA-process is estimated to be as high as 20%[¶].[36] This is supported by observations of TTA upconversion efficiencies exceeding the 5.55 % prediction.[16,23] It is however difficult to measure Φ_{TTA} directly which puts equation (1) to limited use. Therefore, in lack of a more specialized way of calculating upconversion efficiencies, the classical definition of relative quantum yield[37]

$$\Phi_{UC} = \Phi_R \frac{E}{E_R}\frac{A_R}{A}\frac{\eta^2}{\eta_R^{\,2}} \qquad (4)$$

is frequently used and modified in various ways for determining the quantum yield of photon upconversion through TTA systems. In equation (4) Φ is the emission quantum yield, E is the integrated emission, A is the absorbance at excitation wavelength, and η is the refractive index of the solvent. The subscript R denotes the parameters of the reference sample.

An often encountered modification to the classical expression (eq. 4) includes a multiplicative factor of 2 in order to compensate for the 2:1 maximum upconversion efficiency (2 low energy photons are required to get 1 upconverted high energy photon) and assure a maximum quantum yield of unity.

A further modified version of the classic definition of equation (4) is

$$\Phi_{UC} = \Phi_R \frac{E}{E_R} \frac{A_R}{A} \frac{\eta^2}{\eta_R{}^2} \frac{I_R}{I} \frac{h\nu}{h\nu_R} \qquad (5)$$

where I is the light intensity at the excitation wavelength and hv is the energy of the excitation photons. This expression is particularly useful if the reference chromophore is not excitable at the same wavelength as the upconversion sensitizer chromophore. This is applicable when the reference is chosen such that its emission mainly overlaps with the upconverted emission of the annihilator.[32]

Tables 1 and 2 summarize the to-date reported upconversion quantum yields for different TTA-UC systems (Φ_{UC}). It is clear that no standardized method of reporting Φ_{UC} is employed and comparison between systems should be done with caution as in many cases, important details of concentration and/or excitation light intensities are inadequate. The one case where the quantum yield of the same sensitizer-annihilator system has been reported twice[43,44] is a descriptive example of how sensitive the upconversion quantum yield is to various conditions, such as relative concentrations, light intensity and oxygen concentration. Here two groups have studied the PdOEP:DPA system and reported values ranging from >1 % to 16 %.[43,44] It also demonstrates the necessity of accurate reporting of the conditions employed while determining Φ_{UC}. A similar system that has been studied by two separate groups is the PtOEP:DPA system.[48,49] The reported Φ_{UC} values are in good agreement with one another (2.3 % and 2.55 % respectively), even though the relative sensitizer:annihilator concentrations are quite different, 1:280 and 1:28 respectively. However, at identical relative concentrations (1:28) Cao *et al.* did not detect any upconversion.[48] An explanation to these contradictory observations is difficult to find, especially as no comparison between the employed light intensities were possible.

DPA and Pd/Pt porphyrins and derivatives of these are the most commonly used components in polymer and other solvent free systems (table 2). There have also been some impressive quantum yields reported from such systems, close to and in some cases higher than corresponding systems in solution. Recently a DPA and Pt-porphyrin system with hydrocarbon side-chains anchored to the annihilator and sensitizer, respectively, showed an upconversion quantum yield of 14 %,[25] similar to the highest 16 % reported for the DPA and PdOEP pair in fluid solution.[44]

Moving towards a more standardized way of reporting upconversion quantum yields is desirable and thus we suggest using the classical definition of relative quantum yield (eq. 4) and select a quantum yield reference that is excitable with the same excitation wavelength as the upconversion system. Since the reference emission spectrum is unlikely to overlap completely with the upconverted emission spectrum, the wavelength scale should be converted to reciprocal centimeters and the intensities multiplied by the wavelength vector squared to correct for the non-linear relation between emission energy and the wavelength scale.[37] However, we see little reason to include the multiplicative factor of 2 in the quantum efficiency expressions in order to maintain a maximum efficiency of unity. The absolute quantum efficiency of 50% is an intrinsic characteristic of the TTA-upconversion process and should be applied as such. In the cases where it is applicable the reported values in this perspective have been adjusted to correspond to the intrinsic 50 % maximum for better comparison. Given the excitation intensity dependence on the upconversion quantum yield, we also suggest that the quantum yield should be determined through a method using increasingly intense excitation light until reaching the stationary region. The value obtained from this region is considered the upconversion quantum yield of the specific sensitizer/annihilator system. However, it should be noted that the excitation intensity necessary to reach such a stationary regions varies between different upconversion pairs and it will be reached earlier for systems with efficient TET and TTA.[22,29-31] Nevertheless, in most cases this will be beyond the natural intensity of sunlight. This in turn, introduces an unrealistic condition to the quantum yield estimation when considering solar energy applications. In addition, such measurements should always be run at optimal sensitizer:annihilator concentrations as well as under controlled molecular oxygen concentrations. Once again we stress the importance of clear and concise reporting of light intensities and concentrations used for determination of the quantum yield in the stationary region (*vide supra*) to enable a more straightforward comparison between systems.

Besides upconversion quantum yield, also the magnitude of the anti-Stokes shift (ΔE_{UC}) in eV has been reported a number of times in literature.[16,41,47,50,51,61,67,68] However, these reports have often been based on the energy shift between the excitation light peak and the blue-most upconversion emission vibronic peak. Since it is possible to drive upconversion by exciting more or less anywhere in the red absorbing region of the sensitizer, consequently different ΔE_{UC} can be reported for the very same TTA-UC system. We therefore suggest a more standardized method of declaring a possible Upconversion Energy Shift (UES). This would be based on intensity weighted averages of upconversion emission- and sensitizer absorption spectra (on the red side of the upconversion emission) recorded on an optimally composed sensitizer-annihilator system. The spectra should be converted to wavenumbers (*vide supra*). Once the intensity weighted average wavenumber of the upconversion emission ($\bar{\nu}_W^A$) has been calculated, it is used as the upper (blue-side) bound for averaging of the sensitizer absorption. When the averaged wavenumber of the sensitizer absorption ($\bar{\nu}_W^S$) has been derived, the energy-difference between $\bar{\nu}_W^A$ and $\bar{\nu}_W^S$ in eV is reported as UES. For a more detailed explanation see ESI†. This method of reporting UES could further motivate construction of annihilators and sensitizers with their emission and absorption densities respectively more radically separated.

Table 1. Adjusted upconversion quantum yields for various annihilator/sensitizer pairs in solution

Annihilator	Sensitizer	Method	Adjusted[a] Φ_{UC} (%)	Reference
1CBPEA[b]	BODIPY-derivative[c]	eq. 4	0.85	28
BDPPA	PtTPBP	eq. 4	9.3 / 7.3[d]	38
BODIPY-deriv[e]	PtTPBP	eq. 4	~7	39
BPEA	PdTPBP	eq. 5	3.2	32
BPEA	C70	eq. 4	0.4	40
Bis-tetracene	PdTPBP	unspecified	4.0	41
DMA	$[Ru(dmb)_3]^{2+}$	eq. 4	4.0	42
DPA	PdOEP	unspecified	>1	43
DPA	PdOEP	eq. 4	18.0 / 16.0[f]	44
DPA	TIHF[g]	unspecified	0.6*	45
DPA	Pt1[h]	eq. 4	7.05	46
DPA	Pt2[i]	eq. 4	4.45	46
DPA	$[Ru(bpy)_2(Phen)\text{-pyrene}]^{2+}$	eq. 4	4.9	47
DPA	$[Ru(bpy)_2(Phen)\text{ethynyl-pyrene}]^{2+}$	eq. 4	4.8	47
DPA	PtOEP	eq. 4	2.3	48
DPA	PtOEP	integrating sphere	2.55	49
DPA/DPBF	PtOEP	eq. 4	16.0	48
DPBF	PtOEP	eq. 4	4.35	48
PDI	PyrRuPZn2[j]	eq. 4	0.38	50
PDI	PtTPTNP	eq. 4	3.0	51
PDI	H_2TPBP	eq. 4	0.04	52
Perylene	Pt(II)-BODIPY[k]	unspecified	5.2*	53
Perylene	PtTPBP	eq. 4	0.65	54
Perylene	C70	eq. 4	4.25	40
Perylene	PdTPBP	eq. 5	<0.5-5[l]	55
Perylene	PQ_4Pd	unspecified	0.59*	56
Perylene	PPd	unspecified	2.7/4.2*[m]	56
Perylene	BODIPY-derivative[n]	eq. 4	3.05	28
Perylene	BODIPY-derivative[o]	eq.4	8.25	29
Perylene	BODIPY-derivative[p]	eq. 4	5.15	29
Perylene	BODIPY-C60-dyad[q]	eq. 4	3.5	57
Perylene	BODIPY-heterodimer[r]	eq. 4	0.05 / 1.35 / 1.85[r]	58
Perylene	BODIPY-heterodimer[r]	eq. 4	2.45 / 4.0 / 4.05[r]	59
Perylene	BODIPY-Pt(II) complex[s]	eq. 4	5.4	31
Perylene	BODIPY-Pt(II) complex[t]	eq. 4	3.7	31
Perylene	PdTPBP	integrating sphere	0.6	49
Perylene	NDI-drivative[u]	eq.4	9.25	30
Perylene	ZnTPBP	eq. 4	0.16	52
Perylene –BODIPY dyad	ZnTPBP	eq. 4	0.38	52
Perylene-BODIPY dyad	PdTBP	$\frac{\#\ emitted\ photons}{\#\ absorbed\ photons}$	11.3	60
PPO	biacetyl	eq. 4	0.58	26
Rubrene	PdTAP	eq. 5	1.2	61
Rubrene	PtTPTNP	eq. 4	3.3	51
Rubrene	PQ_4Pd	eq. 1[v]	8.0	23

a) Adjusted to correspond to the intrinsic maximum quantum yield of 50 %, in some cases we have not been able to determine the method used for determining the quantum yield thus no adjustment has been made, these values are marked with an asterisk (*). b) 1-chloro-9,10-bis(phenylethynyl)anthracene, c) 2,6'-diiodo-bis-BODIPY dimer, d) 9.3 % reported in article and 7.3 % reported in SI, e) 2,6-diethyl-4,4-difluoro-8-(-4-iodophenyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene, f) 32 % measured, 36 % recalculated without reabsorption, g) 2,4,5,7-tetraiodo-6-hydroxy-3-fluoron, h) dbbpy Pt(II) bis(coumarin acetylide) i) dbbpy Pt(II) bis(phenylacetylide), j) ruthenium(II) [15-(4′-ethynyl-(2,2′;6′,2″-terpyridinyl))-bis[(5,5′,-10,20-di(2′,6′-bis(3,3-dimethylbutoxy)phenyl)porphinato) zinc(II)]ethyne][4′-pyrrolidin-1-yl-2,2′;6′,2″-terpyridine]bis(hexafluorophos-phate), k) BODIPY-bis-N^C^N Pt(II)–Acetylide Complex, l) Φ_{UC} varying in different ionic liquids, m) at 4 W/cm^2 and 20 W/cm^2 respectively, n) 2-iodo-6-ethynyltrimethylsilyl-1,3,5,7-tetramethyl-8-phenyl-4,4-difluoroboradiazaindacene, o) 2-monothienyl-BODIPY, p) 2,6-dithienyl-BODIPY , q) bis-BODIPY-C60-dyad, r) for varying BODIPY-heterodimer sensitizers, s) diimine Pt(II) acetylide-BODIPY complex , t) diimine Pt(II) acetylide-phenyl-BODIPY complex, u) napthalenediimide-derivative, v) With $\Phi_{TET}=1$, $\Phi_{A,f}=0.8$ and $\Phi_{s,ISC}=1$.

Table 2. Adjusted upconversion quantum yields for various annihilator/sensitizer pairs in non-solution conditions

Annihilator	Sensitizer	Method	Adjusted Φ_{UC} (%)^a	Condition	Reference
alkyl-DPA	alkyl-PtP	eq. 4	14	Solvent free	25
DPA	PtOEP	integrating sphere	1.15	In liposome	49
DPA	PdOEP	eq. 4	10.35	In CLRFX polymer	24
DPA	PtOEP	eq. 4	14	In HD/PIB	62
DPA	PtOEP	unspecified	0.02*	In PMMA	63
DPA	PtOEP	modified eq. 5	3.0×10^{-4}	On ZrO_2 NP	64
DPA	PtOEP	eq. 4	3.0	Cross-linked ps-NP in solution	65
DPA	PtOEP	integrating sphere	3.7	Cross-linked ps-NP in film	65
Perylene	PdTPBP	eq. 5	2.4	In micelle	66
Perylene	PdTPBP	integrating sphere	0.25	In liposome	49

a) Adjusted to correspond to the intrinsic maximum quantum yield of 50 %, in some cases we have not been able to determine the method used for determining the quantum yield, thus no adjustment has been made, these values are marked with an asterisk (*).

Demonstration devices

The interest in utilizing photon-upconversion in solar energy applications has increased during recent years. There have been a number of theoretical estimations on possible efficiency increase regarding photon-upconversion assisted solar cells.[20, 69-71] For an ideal TTA based intermediate band solar cell (1.7 eV) it was found that the maximum power conversion efficiency could be increased from 28.8 % to a maximum of 43.6 %.[20] A detailed review on upconverter solar cells and their applications was published in 2011 by de Wild *et al.*[10] By that time, only a few photovoltaic devices with upconversion materials had been demonstrated and they were all based on rare earth metal ions (in particular lanthanide ions) upconversion (RE-UC). Today the situation is different, since 2011 there have also been examples of upconversion devices based on TTA occurring in organic chromophores.

The lanthanide based upconversion systems typically possess an absorption toward the IR region of the solar spectrum.[10] The absorption coefficient of these systems is quite low and narrow as they rely on forbidden f-f transitions.[37,72] Recent attempts to increase the efficiencies of the RE-UC and alter the quantum yield, consist of both chemical and physical approaches.[73,74] In contrast, the light absorbing species in TTA-UC systems are organic molecules or metalorganic compounds with good absorption up to the NIR.[16,29-32,39,41,50,51,54,61] The record anti-Stokes shift of a TTA-UC system is 0.94 eV for the palladium tetrakisquinoxa-linoporphyrin (PQ_4Pd) sensitizer and perylene emitter couple (Figure 1).[56] It has also been demonstrated that TTA-UC works efficiently even under low intensity, non-coherent, sunlight irradiation,[32,41,43,67] contrary to other upconversion techniques. UC techniques based on RE ions and TTA are optimal at different wavelengths and it might be suitable to combine the two, rather than to choose one and dismiss the other, when optimizing a device.

Solar energy applications that can benefit from upconversion can be generalized into two different types of applications. The first obviously being photovoltaic devices, and specifically third generation PVs, that typically have higher band-gaps compared to c-Si solar cells. Secondly, upconverted photons from sunlight can be used to drive photochemical reactions that require high-energy photons to proceed. In the last few years there has been a markedly increase in proof-of-principle devices demonstrating the possibility of employing UC in solar energy related applications. In particular the integration of UC in photovoltaics and photocatalytical devices

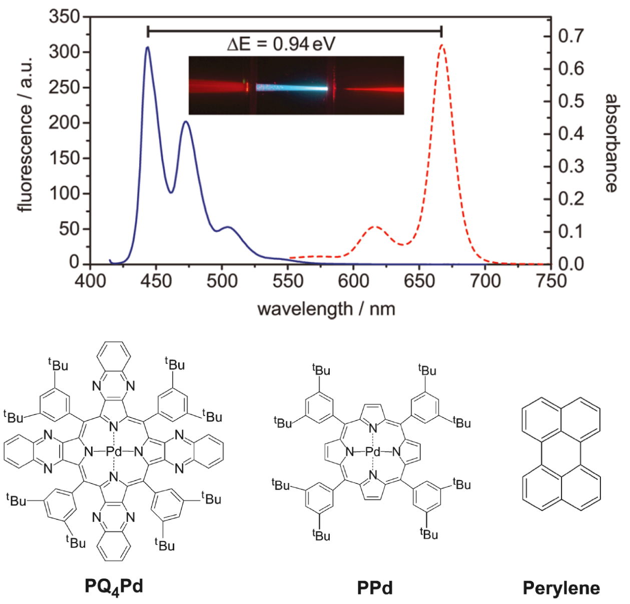

Figure 1. Normalized absorption and emission of perylene and PQ_4Pd (top) and structure of PQ_4Pd and perylene (bottom). Reprinted (adapted) with permission from Cheng et al., *J. Phys. Chem. A*, 2011, **115**, 1047–1053. Copyright (2011) American Chemical Society.

has been studied theoretically and practically. Also the possibility of using upconverted photons from white light to drive chemical reactions has been demonstrated.[62,75,76]

The TTA efficiency has, at low intensities, a quadratic intensity dependence.[21-27] With current systems this means that at standard external quantum efficiency (EQE) characterization experiments, for solar cells, the illumination intensity is too low to generate any noticeable UC enhanced signal[77] To circumvent this, one can use concentrated sunlight or pump the UC part with a laser to generate a background triplet concentration and probe with low intensity white light. However, with this approach follows a general problem when assessing and comparing the efficiency enhancement of the devices, as the efficiency is greatly increased at higher intensities.

TTA-UC in Photovoltaics

All third generation photovoltaics (PVs) suffer from high band-gaps compared to c-Si and thus transmit a large fraction of the low energy photons in the solar spectrum. Integrating UC in such devices can theoretically increase the efficiency up to 43.6 %.[16] Schmidt and co-workers have demonstrated a number of UC integrated PV systems, including a-Si:H,[67,68] organic photovoltaics (OPVs)[67] and dye sensitized solar cells (DSCs).[69] In order to be able to compare the efficiency enhancement between these devices Schmidt and co-workers introduced a figure of merit (FoM), ζ which is the total short circuit current density increase of a solar cell, normalized by the square of the solar concentration (C)[§] and thus has the unit of $[\mathrm{mA\ cm^{-2}\ \odot^{-2}}]$.[77,78] The total short circuit current density increase can be calculated from the measured external quantum efficiency (EQE) difference between the PV cell and the UC assisted PV cell as described in equation 6:

$$\Delta J_{SC}^{UC} = Ce \int \Phi_{\mathrm{AM1.5G}}(\lambda) \times \Delta EQE_{UC}(\lambda) d\lambda \qquad (6)$$

where e is the elementary charge, C the solar concentration factor and $\Phi_{AM1.5G}$ is the AM1.5 solar flux in photons per area time per wavelength. This then gives $\zeta = \Delta J_{SC}^{UC} / C^2$.[77,78]

Table 3 shows a comparison of ζ for different types of solar cells with and without back reflectors and between TTA-UC and RE-UC. The components of the TTA systems in these studies were rubrene as acceptor and tetrakisquinoxalino-porphyrin (PQ_4Pd) or nitroaminopalladiumtetrakis porphyrin (PQ_4PdNA) as sensitizers. The maximum UC efficiency for the former system has been determined to be 8.0 %.[23] In order to achieve a wavelength dependent response of the generated current enhancement a laser diode (670 nm, matching PQPdNA absorption) was used to pump the UC layer while measuring the EQE.

The first fully integrated TTA-UC PV device was reported recently by Nattestad et al.[80] and consisted of a dye sensitized solar cell (DSC) architecture similar to a tandem-DSC where the second active layer instead consisted of an UC-fluid (Figure 2). The reported FoM of this un-optimized device (2.5×10^{-4} $\mathit{mA\ cm^{-2}\ \odot^{-2}}$) lies between those of the OPVs and the best α:Si-H PV (Table 3).[80]

TTA-UC for chemical reactions

Beyond improving PV efficiencies, TTA-UC can also be used to enable photochemical reactions requiring high photon energy to be driven by sunlight. Only a few examples of this have been reported so far. As many photochemical reactions require high energy UV photons, which are relatively scarce in the natural solar spectrum, the relative UC photoresponse is consequently greater for these devices than that of PVs. It is also relatively straightforward to filter out the high energy photons from the light source in order to qualitatively demonstrate the effect of the UC. Therefore photochemical UC enhanced devices are suitable for demonstrating proof-of-principle UC systems. However, direct comparison between these devices is difficult as the efficiency depends on the setup and the system itself.

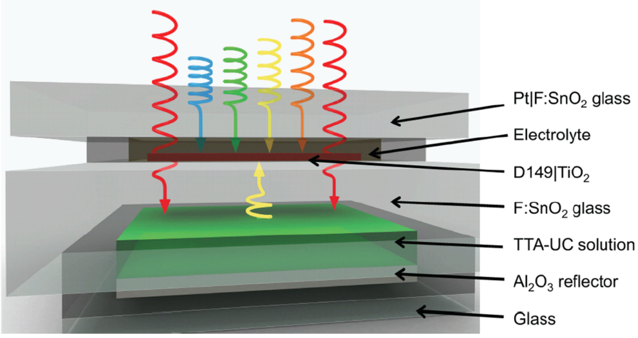

Figure 2. A schematic illustration of the TTA-UC integrated DSC. Low energy photons pass through the electrolyte/dye layer and are absorbed by the UC solution where they are upconverted and reemitted. Reprinted with permission from Nattestad et al. *J. Phys. Chem. Lett.*, 2013, 4, 2073–2078. Copyright (2013) American Chemical Society.

In 2006 Islangulov and Castellano demonstrated that bimolecular [4+4] cycloaddition between two anthracene molecules was possible even when exciting at 457.9 nm – 532 nm, light that anthracene itself does not absorb but the triplet sensitizer $[Ru(dmb)3]^{2+}$ does.[75] In this study there was no need for the acceptor to emit a photon, as it is the singlet-excited acceptor produced in the annihilation step that reacts further. One can envision this procedure representing a larger group of synthetic applications where reactions requiring high-energy UV photons can be powered by visible light. Either where the produced excited singlet acceptor is the reacting species, as above, or where the emitted photon from the excited singlet acceptor in turn excites the reacting specimen. The later example was recently demonstrated with a Pt /WO_3 photocatalyst with a band gap of 2.8 eV, which produced •OH, when irradiated by sub-bandgap photons.[62]

Table 3. Comparison of upconversion enhanced PV devices

Device Type	Type	C ($\odot$)	*ζ (mA cm^{-2} $\odot^{-2}$)*	Reference
P3HT:ICBA[a]	TTA	17.3	1.60×10^{-4}	77
PCDTBT:$PC_{71}PM$[a]	TTA	28.9	1.54×10^{-4}	77
a-Si:H (p-i-n)	TTA	19	7.63×10^{-4}	77
a:Si:H (p-i-n)	TTA	48.3	1.3×10^{-4}	78
a-Si:H (p-i-n)[b]	TTA	24	3.5×10^{-4}	79
DSC	TTA	3	2.5×10^{-4}	80
a-Si:H (p-i-n)	RE[c]	790	0.066×10^{-5}	81
Si	RE[d]	210[e]	3.0×10^{-4}	82

[a] OPV, [b] with Ag-sphere back reflector, [c]β-$NaYF_4$:Yb^{3+} (18%), Er^{3+} (2%) with white back reflector, d)β-$NaYF_4$: Er^{3+}(25%) PTFE as rear diffuse reflector, e) estimated from geometrical considerations.

There has also been proof-of-principle device were water splitting was achieved in a photoelectrochemical cell driven by upconverted photons.[44] Even though the WO_3 photoanode and the cuvette, containing the DPA/PdOEP upconversion fluid, were not optically and geometrically optimized a generated photocurrent was observed when the UC fluid was degassed.

No current was observed for the aerated samples, which corresponds to the case without UC.

Another example of an UC enhanced photochemical reaction was reported by Börjesson et al. where the photoisomerization of a fulvalene diruthenium derivative ($FvRu_2$) was driven by blue photons upconverted from truncated white light.[76] In the study two microfluidic chips were placed on top of each other, the $FvRu_2$ containing liquid was pumped through the top channel and an upconversion fluid consisting of diphenylanthracene (DPA) and palladium octaethylporphyrin (PdOEP) in toluene was pumped through the bottom channel. Comparison between experiments with and without upconversion showed a 130 % increase in conversion of the photo-isomer when upconversion was used.

The *trans* to *cis* isomerization of azotolane has also been initiated by upconverted light.[38] Azotolane was incorporated into a photodeformable matrix (cross-linked liquid-crystal polymer, CLCP) with a polyurethane top layer containing the upconversion materials (PtTPBP/BDPPA). When irradiating the top UC layer the subsequently emitted blue light activated the photoisomerization, the structural change in turn resulted in the bending of the CLCP matrix towards the light source. This is an interesting example of a photo-reaction driven by upconverted light, which results in a mechanical effect.[38]

Conclusions

With this perspective we have reviewed recent progress in the field of triplet-triplet annihilation photon upconversion in solar energy applications and suggested a general way to evaluate the performance of photon upconversion systems. The efficiency of photon upconversion processes has improved considerably during recent years. The demonstrated TTA-UC efficiency has increased from a fraction of a percent to more than 16 %[28] under ideal experimental conditions. The increased efficiency of the systems, together with demonstration of increased photostability[25] makes us very optimistic about the future development of functional devices that utilise photon upconversion under practical conditions.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Description of the TTA process, derivation of Eqs. (2) and (3) and detailed explanation of Upconversion Energy Shift determination.

¶ Value adjusted to correspond to the intrinsic 50 % quantum yield.

§ The concentration factor is the equivalent number of suns corrsponding to the used light intensity, where 1 sun corresponds to standard illumination at AM1.5, ⊙.

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