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Perspective

Harnessing Sunlight via Molecular Photon Upconversion

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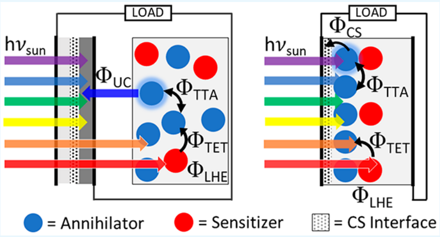
ABSTRACT: Molecular photon upconversion via triplet−triplet annihilation (TTA-UC) is an intriguing strategy to harness sub-bandgap photons and surpass the Shockley−Queisser (SQ) limit for solar energy conversion. In this perspective, we briefly summarize the progress to date harnessing TTA-UC in solar cells using both optically and electrically coupled schemes. We then highlight the efficiency limiting processes for these schemes and outline possible paths toward upconverted photocurrent contributions of >1 mA/cm^2. Further progress in red-shifting absorption, coupling to high-energy light harvesting motifs, photon management, sensitizer/annihilator design, and more are necessary for the realization of a viable TTA-UC solar cell that can pass the SQ limit.



KEYWORDS: *photon upconversion, solar cells, triplet−triplet annihilation, quantum yield, photocurrent*

Photon upconversion (UC) is the process of combining two or more low energy photons to generate a higher energy excited state and offers a means of pushing the maximum theoretical limits of single junction solar cells from 33% to >45%.[1] Of the strategies, molecular UC via triplet−triplet annihilation (TTA) is particularly appealing, because TTA efficiencies of >30% (Φ_{TTA} = # of singlet excited states/# of triplet excited states)[2] can be achieved and it is efficient under noncoherent, solar intensities.[3,4] Previous estimates indicate that coupling even a 20% efficient TTA-UC scheme to a 22% efficient perovskite solar cell, for example, could increase the short circuit current (J_{sc}) and power conversion efficiencies (PCE) by ∼2.5 mA and ∼2 percentage points, respectively.[5]

Since the first report of utilizing TTA-UC for sunlight to electrical conversion in 2012,[6] notable advancements have been made in harnessing the photocurrent contribution from UC (J_{UC}), with the progress to date summarized in Figure 1.[6−20] This graph includes *device relevance* and *device impact* thresholds, which are roughly the minimum J_{UC} to overcome PCE measurement uncertainties (0.1 mA/cm^2) and a >1 percentage point increase in PCE (1.0 mA/cm^2), respectively.[5,21]

Figure 1 also partitions the performance outcomes into the two primary strategies for harnessing TTA-UC: optically (in gray) and electrically (in red) coupled schemes. A general depiction of both strategies is shown in Figure 2. Briefly, in the optically coupled scheme, an UC solution or film is used in conjunction with a standard solar cell.[6−8,10,11] Sub-bandgap light is transmitted through the solar cell, absorbed by a TTA-UC solution or film, upconverted, and then emitted photons are directed back at the solar cell. For the electrically coupled scheme, the sensitizer (S) and annihilator (A) pair are incorporated into the solar cell. The low energy light is absorbed by S, the triplet state transferred to A, then following TTA but prior to emission, the upconverted state is charge-separated (CS) and the charge-collected at the electrodes.

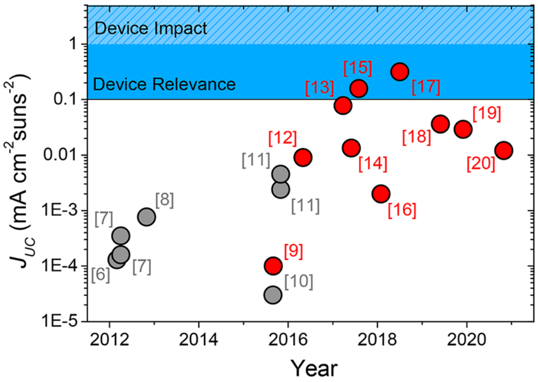


Figure 1. Progression in photocurrent contribution from TTA-UC under 1 sun intensity (AM1.5) (reference numbers are given in brackets) with optically and electrically coupled schemes in gray and red, respectively.

Noting that the *y*-axis of Figure 1 is on a log scale, significant progress has been made with both strategies over the past decade, but we are still yet to reach the device impact threshold. Herein, we discuss the limitations of current TTA-

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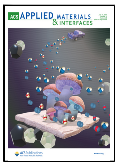

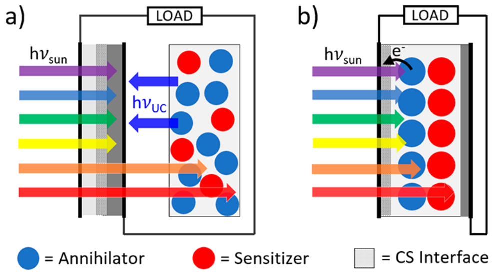

Figure 2. A general depiction of (a) optically and (b) electrically coupled strategies for harnessing TTA-UC in a solar cell with the sensitizer and annihilator molecules depicted in red and blue, respectively (CS = charge separation).

UC solar cells as well as outline possible steps forward to increase J_{UC} and enhance the impact of TTA-UC on solar cell performance.

Despite their differences, both schemes can benefit from progress in chromophore design like (1) new sensitizers with long triplet lifetimes and high extinction coefficients from 700 to 1000 nm, (2) new annihilator molecules with low nonradiative rates, optimized singlet−triplet gaps, and high TTA yields (i.e., minimal losses via the triplet and quintet TTA decay channels), and (3) appropriate energetic matching between new S-A pairs. Even using current materials/strategies, these advances will help to improve low-energy light-harvesting efficiencies (Φ_{LHE}), increase the upconversion quantum yield (Φ_{UC}), and decrease the maximum TTA efficiency onset threshold (i.e., the I_{th} value).[22] However, these schemes also have distinct limitations that require unique materials design and engineering solutions.

The optically coupled scheme is arguably the more straightforward of the two strategies and offers several notable advantages, including (1) it can build upon already available, high efficiency solar cells, (2) the solar cell and TTA-UC components can be independently designed/tuned, (3) any of the already available UC emission materials can be used, and (4) only excited-state energies, and not redox potentials, of the S and A are a concern.

Unfortunately, the highest J_{UC} reported to date for an optically coupled scheme is below 0.1 mA cm^{-2}. The low photocurrent can be attributed to several factors (Figure 3).

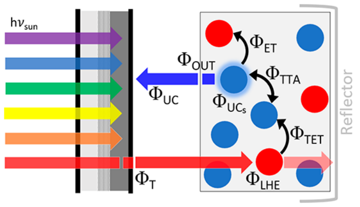

Figure 3. Diagram depicting the events and quantum yields for TTA-UC in an optically coupled UC solar cell.

First, while sub-band gap light readily transmits through the active solar cell material, the remainder of the device (i.e., blocking layers, the electrical contact, and substrate) are not optimized for low energy or upconverted light transmission, so 60% or more of photons are absorbed and lost as heat ($\Phi_T < 0.4$).[8] While some transmission losses are inevitable, attempts to optimize light transmission are limited, so there is ample opportunity for improvements, in terms of both materials selection and solar cell optimization.

Second is the TTA-UC efficiency of the films. The highest upconversion emission quantum yields (Φ_{UC}) reported to date are on the order of 38% ($\Phi_{UC(max)} = 50\%$) but are achieved in solution.[3] Because of issues such as solvent evaporation, solid-state UC films are the more practical option but suffer from notably lower Φ_{UC} (11%),[23] primarily because of decreased molecular mobility hindering energy transfer and TTA. But progress has been made using solid-state materials with increased mobility and/or triplet migration in polymers, gels, self-assembled motifs, nanocapsules, and more.[24−26] Further increases in Φ_{UC} with materials design will directly translate to increased J_{UC}.

However, achieving high efficiency for generating the upconverted state (Φ_{UCs}) is not enough. We must also minimize $^1A^*$ to S back-energy transfer (Φ_{ET}) and maximize the photon output coupling yield (Φ_{OUT}) from the UC film to the solar cell. Φ_{ET} is dictated by the overlap integral for the emission of $^1A^*$ and absorption of S and the concentration of the sensitizer. Porphyrins are a popular choice for S because of the transmission window between the Soret- and Q-bands minimizes the spectral overlap with $^1A^*$ emission. However, at high S concentrations, even a small overlap integral can lead to significant losses, because of Φ_{ET}. Consequently, the need for high S concentrations for maximized external light-harvesting efficiencies (Φ_{LHE} = # S*/# of incident photons) must be weighed against losses due to Φ_{ET}. Also noteworthy is the fact that systems with increased triplet mobilities are favorable for TTA but they also typically increase singlet mobilities and Φ_{ET}. Some of these losses can be mitigated using an additional singlet sink or collector molecule that emits from the singlet excited states but they do inherently lead to energy losses.[27,28]

Φ_{OUT} is the fraction of UC photons generated that exit the upconversion film toward the solar cell. Decreases in Φ_{OUT} can be due to scattering, waveguiding, and inner filtering by A/S, which are architecture-dependent phenomena. For example, since UC emission is isotropic, a back reflector must be included to direct photons toward the solar cell.[8,29] Analyses show that the incorporation of a Lambertian reflector and optimized UC film thickness can increase J_{UC} by a factor of 6-fold or more.[21] Improved reflector design combined with new sensitizers with increased extinction coefficients and decreased overlap integrals are key steps toward decreasing Φ_{ET} and increasing Φ_{OUT}.

Accounting for reasonable improvements on all of these fronts, device-relevant J_{UC} values (>1 mA/cm^2) are attainable with an optically coupled TTA-UC solar cell scheme.[21]

As an aside, an optically coupled, solar concentrator/waveguide strategy for harnessing TTA-UC in a solar has recently been reported.[30−32] However, the J_{UC}-only contribution was not measured and their overall performance were reported in terms of device area (i.e., not area of irradiation) so the outcomes were not included in Figure 1. Nonetheless, many of the losses and proposed improvements noted above, except for solar cell transparency, apply to TTA-UC waveguides as well.

The electrically coupled TTA-UC scheme also has distinct advantages and disadvantages. First, they do not rely on upconverted photon generation, so concerns with photon management, nonproductive back ET, and sensitizer concentration are diminished. Second, typically the S's and A's are in proximity, which decreases diffusion-related Φ_{ET} limitations. Finally, photocurrents of >0.3 mA/cm^2 have already been demonstrated under 1 sun intensities.[17]

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On the other hand, these are entirely new solar cell architectures that will require significant optimization in both performance and production if they are ever to be commercially viable. Additionally, since charge separation is required, not only are excited-state energetics a concern but also redox potentials, which introduces additional demands/restrictions on sensitizer and annihilator design. The device is also inherently more complex enabling new loss pathways. We are effectively requiring these devices to be good at both TTA-UC and photocurrent generation, each of which is a nontrivial challenge.

To date, TTA-UC has been incorporated into both dye-sensitized solar cells (DSSCs)[9−13,15−20] and organic photovoltaic (OPV)[14] device architectures, as well as a proof-of-concept hybrid film.[33] The DSSC motif is most common with heterogeneous, codeposited, and metal-ion-linked architectures shown in Figure 4.

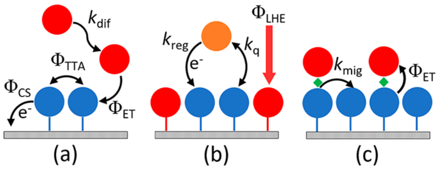

Figure 4. Generic depiction of (a) heterogeneous, (b) codeposition, and (c) metal-ion-linked strategies for harnessing TTA-UC in a DSSC. The redox mediator is shown in orange.

In all examples to date, A is directly adhered to mesoporous TiO_2 via $-COOH$ or $-PO_3H_2$ binding groups. Direct binding has the advantage of facilitating subpicosecond charge separation (Φ_{CS}) of the UC state, which outcompetes losses due to excited-state decay or back ET.[34] However, it requires synthetic modification of A molecules with surface binding groups. Also, in contrast to the isotropic orientation in a host medium, surface binding introduces geometric restrictions that can help or hinder electron transfer, energy transfer, and TTA events.[20,35] Understanding and controlling these orientation-dependent events will be a crucial step in increasing the efficiency of triplet migration (k_{mig}) and TTA.

The primary difference between the strategies in Figure 4 is the sensitization mechanism. For the heterogeneous scheme (Figure 4a),[9,16] S is in the electrolyte solution, so it does not require surface binding groups, but TET is diffusion-limited (k_{dif}). Co-deposition (Figure 4b) has the advantage of S—A proximity[18] but the concentration of each is surface- range of 100%-limited, which can affect the light harvesting efficiency. In addition, the presence of S decreases the packing density of the A layer, which may hinder triplet migration across the surface.[36] The metal-ion-linked strategy, maximizes both A and S loading and fixes the molecules in proximity (Figure 4c). It also enables the formation of triplet-sensitized[13] and singlet-sensitized[17] trilayers. However, this scheme requires A to have geometrically opposed binding groups and orientation-dependent interactions between S and A that are intrinsic to the scaffolding.

Also shown in orange in Figure 4b is the redox mediator, which is necessary in DSSCs to regenerate the oxidized dyes and close the circuit. Unlike in traditional DSSCs where the excited states are quickly harvested via charge separation, TTA relies on long-lived triplets prior to UC. Consequently, we must be conscientious of regeneration (k_{reg}) and excited-state quenching dynamics (k_q).[15] All devices to date have used either I^-/I_3^- or $Co^{III/II}$ polypyridyl mediators, so there is much to be learned and still significant room for improvement with new mediators including solid-state hole transport materials.

Finally, and perhaps the largest hurdle for TTA-UC DSSCs, is efficiently harnessing the high energy photons. In fact, the strategy comparison in Figure 1 is slightly misleading in that the optically coupled J_{UC} is a complement to an already efficient solar cell, whereas the electronically coupled devices only focus on low-energy light harvesting. The annihilator molecule can harness high energy light but for this device to push efficiency limits, it must perform on par with the best DSSCs to date (i.e., broad absorption, efficient injection, etc.) and there must be no competitive high energy absorption from S. The former is a lot to ask from A (i.e., efficient TTA and PCE), the latter may be physically impossible. The much more likely solution, originally proposed by Dilbeck et al.,[5] is to generate a layered metal oxide anode where the top, scattering layer of a record perovskite or DSSC is replaced by an upconversion layer. Layered devices like these are known[37] but are yet to be implemented in TTA-UC DSSCs.

In 2017, Lin et al. published the first example that harnesses TTA-UC in an OPV.[14] A general depiction of their device architecture can be seen in Figure 5 and was composed of S doped into a layer of A with C60 as the electron acceptor/charge separation layer.

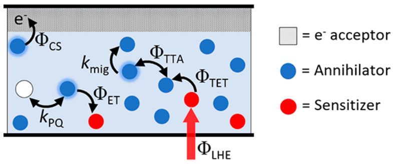

Figure 5. Device structure of an OPV-based TTA-UC solar cell.

The J_{UC} for this particular device was relatively low (13 μA cm^{-2}) but one can envision several advantages of this architecture. These include (1) S doping can be controlled during vapor deposition, (2) S and A are in close contact for efficient TET, (3) in terms of fabrication/commercialization, it is a known architecture, and (4) known TTA pairs can be used without synthetic modification. There are also several notable disadvantages. First is that it relies on random walk migration of triplet and singlet excited states to the annihilation event and charge-separation interface, respectively. This can lead to decreased Φ_{TTA} and losses due to polaron quenching (k_{PQ}) but could be minimized with improved exciton/polaron transport. The random migration combined with S and A proximity also allows for $^1A^*$ to S back energy transfer (Φ_{ET}) especially at high S concentrations (i.e., high Φ_{LHE}). To remedy these issues, the authors suggest a triplet energy cascade architecture where a triplet accepting host for S is independent of the A layer which could minimize back ET and keep $^1A^*$ in proximity to the charge separation interface. Finally, there is still the issue of efficiently harnessing high energy photons which would again require no competitive absorption by S or the triplet host, or an entirely new architecture where high energy photons can be absorbed/harnessed prior to the TTA-UC materials.

In summary, much progress has been made in harnessing TTA-UC for solar energy conversion, but further improvements are needed in order to achieve device relevance

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thresholds and eventual application. While there are many unknowns and challenges ahead with TTA- UC solar cells, there is little doubt that even with currently available materials and strategies, performance optimizations would lead to J_{UC} values of >1 mA/cm^2. Further improvements in red-shifting absorption, coupling to high energy harvesting motifs, photon management, and more are imminent and will rely on the intersection of chemical, materials science, and engineering knowledge and innovation.

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Notes

The authors declare no competing financial interest.

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