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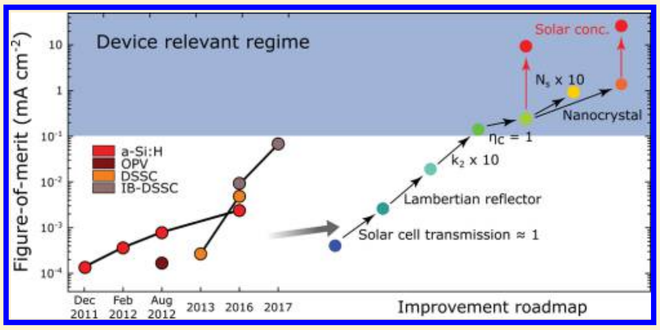
PERSPECTIVE

Optimizing the Efficiency of Solar Photon Upconversion

Laszlo Frazer, Joseph K. Gallaher, and T. W. Schmidt*

ARC Centre of Excellence in Exciton Science, School of Chemistry, University of New South Wales, Sydney, New South Wales 2052, Australia

ABSTRACT: **Low-energy photons, which are not used by a solar cell, can be converted to higher-energy photons by photon upconversion. The figure-of-merit of upconvertors, J_{UC}, is given in mA cm^{-2} under 1 sun excitation conditions. A device-relevant J_{UC} should not be less than 0.1 mA cm^{-2}. However, to date, the highest J_{UC} reported is in the 10^{-2} mA cm^{-2} range. In this Perspective, we analyze the shortcomings of previously reported devices and unfold a roadmap toward device-relevant, high-efficiency upconvertors.**



Photovoltaics have become a significant contributor to power generation in many places around the world.[1,2] Ultimately, it is desirable to extract as much energy from the solar spectrum as possible, especially where there are area constraints. However, a single-threshold solar cell can only extract a maximum of 33.7% of the standard solar spectrum as electrical energy,[3,4] with the most significant efficiency losses owing to thermalization of the photon energy above the bandgap and the transmission of photons with energy lower than the bandgap.[5] Addressing just one of these losses raises the maximum efficiency of quantum solar energy converters (as opposed to solar thermal) above 40% under nonconcentrated sunlight and over 50% for concentrated sunlight.[4,6−8]

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In the past decade, there has been progress made in the application of upconversion to solar cells.[6,9−24] Upconversion is a process whereby absorption of lower-energy photons results in the emission of higher-energy photons. There are two distinct brands of upconversion: those based on energy levels of lanthanoid ions[25−27] and photochemical upconversion (PUC).[28−39] This Perspective focuses on the latter.

In any upconversion scheme, the energy must be stored for long enough to interact with another quantum of energy. This is also the case for the intermediate band cell and has been termed a "photon ratchet".[4,40−43] Relaxations between each step of the ratchet have been shown necessary for efficient operation of upconvertors and intermediate band solar cells.[6] Indeed, the voltage in the terminals of a single-threshold solar cell functions as a ratchet, mitigating radiative recombination. In lanthanoid ion upconversion, there is no ratchet at the first absorption step, and as such, it is inherently less efficient than PUC.

PUC proceeds with absorption of low-energy photons by a sensitizer species. In most studies, the sensitizer undergoes intersystem crossing to a long-lived triplet spin state, and this energy is transferred by a Dexter process[44] to an emitter species, either directly or through an intermediary "transmitter".[15,38] These energy transfers constitute the ratcheting mechanism. With the absorbed photon energies pooled as triplet excited states of the emitter, the triplets can then annihilate to generate emissive singlet spin states. The subsequent sensitized P-type delayed fluorescence[45] is at a shorter wavelength than the absorbed light and can be used for irradiating a solar cell. The process is illustrated in Figure 1.

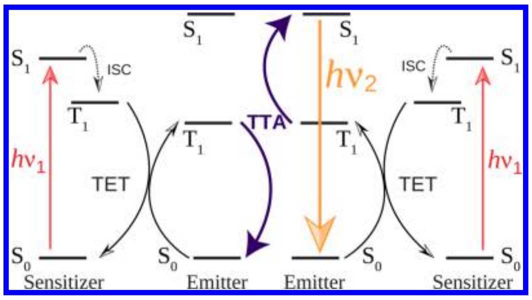

Figure 1. Energy transfer processes giving rise to PUC by triplet−triplet annihilation.

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The applications of PUC have been confined to high-threshold solar cells such as amorphous silicon,[9−11,15] bulk heterojunction,[11] and dye-sensitized cells.[12,15,46−49] The prevailing figure-of-merit J_{UC} for such devices is the short-circuit current increase, owing to upconversion, under 1 sun illumination,[9] or, in the case that the conditions are greater than 1 sun, the current is to be divided by the square of the concentration factor to reflect the quadratic dependence of the process. Quadratic scaling can be assumed when triplet−triplet annihilation is inefficient. The progress of PUC as applied to solar cells is summarized in Figure 2. The highest recorded figure-of-merit is 7.41×10^{-2} mA cm^{-2}, measured at 1 sun.[46−48] This is well below a device-relevant figure of 0.1 mA cm^{-2}. In our view, 0.1 mA cm^{-2} is sufficient to exceed measurement uncertainties commonly encountered when testing solar cells.

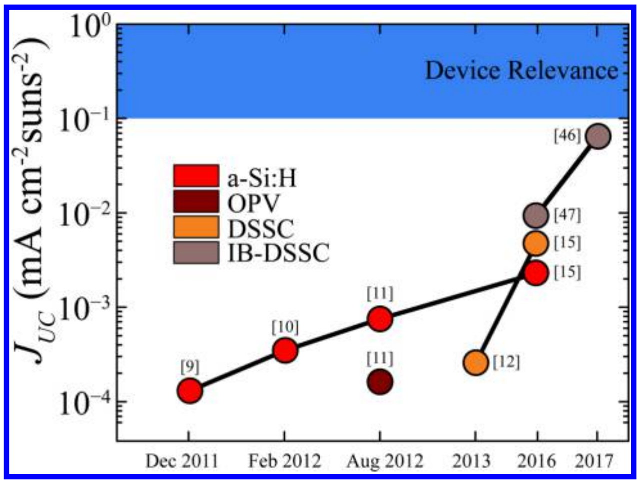

Figure 2. Evolution of the reported figure-of-merit. Above 0.1 mA cm^{-2} under 1 sun illumination, the upconversion current can be considered device-relevant. Results are shown for amorphous silicon (a-Si:H), organic (OPV), dye-sensitized (DSSC), and intermediate band dye-sensitized (IB-DSSC) upconverting solar cells.

The measured J_{UC} can be improved by many strategies:

1. The solar cell itself can be improved.
2. The transmission of the solar cell below threshold can be improved.
3. The light trapping optics can be improved.
4. The absorption spectrum of the upconvertor device can be broadened.
5. The inherent efficiency of the upconversion process can be improved.

In this Perspective, we unfold a roadmap of the route toward an efficient PUC solar cell by use of a stochastic simulator of upconversion. We address each of the above factors in turn to estimate the effect on the J_{UC}. We begin with a description of upconversion kinetics and the results of simulations for upconvertors that are deep enough that back surface effects can be neglected and that lack any ancillary sunlight concentrating optics.

We first model a rubrene upconvertor sensitized with the PQ$_4$PdNA porphyrin previously reported[9,50,51] (structures shown at the top of Figure 3). The emitter and sensitizer are matched reasonably well spectrally, as shown in Figure 3. Rubrene emission largely occurs in the transmission window afforded by the gap between the Q and Soret bands of the porphyrin species. We use the solar spectrum with normal incidence subjected to a 600 nm long-pass filter to represent the transmission of a high-threshold solar cell. Using a porphyrin concentration of $N_S = 1 \times 10^{-3}$ M (6×10^{17} cm^{-3}), we calculate that the 1 sun excitation rate at the front of a planar upconvertor is $k_\phi N_S = 3.49 \times 10^{18}$ cm^{-3} s^{-1}. We choose these units rather than chemistry units of moles and liters because they are immediately compatible with those used by device engineers and scientists. The rate of excitation between 600 and 1000 nm per sensitizer molecule, k_ϕ, is thus about 6 s^{-1}, which is a ballpark figure worth committing to memory.

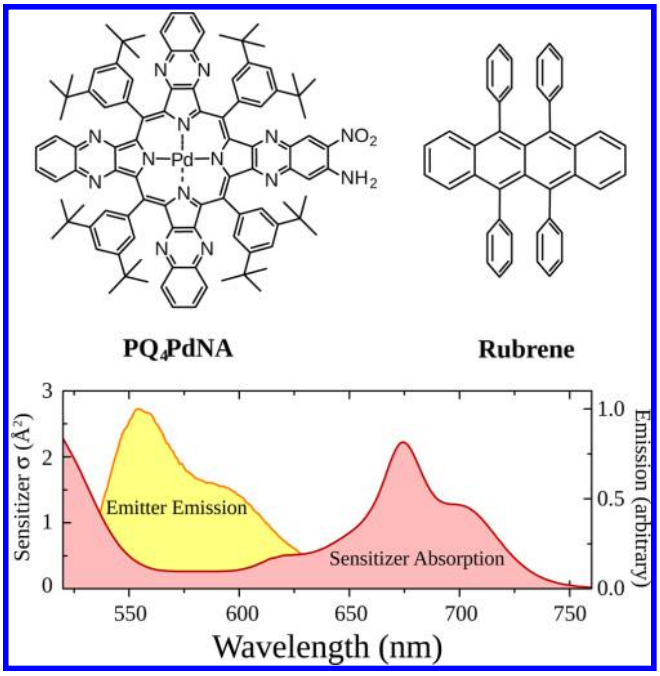

Figure 3. (top) Typical sensitizer (PQ$_4$PdNA) and emitter (rubrene) species. (bottom) Absorption spectrum of PQ$_4$PdNA, compared with the emission spectrum of rubrene. The window in the absorption spectrum allows a large proportion of rubrene fluorescence to escape the upconversion medium.

We estimate the efficiency of the upconvertor at the front of the sample by using a quadratic equation describing the steady-state kinetics of the photochemistry

$$\dot{N}_T = 0 = k_\phi N_S - k_1 N_T - k_2 {N_T}^2 \tag{1}$$

assuming efficient and rapid intersystem crossing and subsequent triplet energy transfer. Choosing realistic figures of $k_1 = 10^4$ s^{-1} for the decay rate of noninteracting triplets and $k_2 = 1.7 \times 10^{-13}$ cm^3 s^{-1} for the triplet−triplet annihilation constant,[35] we arrive at a triplet concentration of $N_T = 3.27 \times 10^{14}$ cm^{-3}. The maximum photon production rate at the front of the upconvertor is thus

$$\begin{aligned} W_{UC} &= \Phi_F \frac{\eta_c f_2 k_\phi N_S}{2} \\ &= 2 \times 10^{16} \text{ cm}^{-3} \text{ s}^{-1} \end{aligned} \tag{2}$$

where f_2 is the proportion of triplet decay due to second-order events, $f_2 = k_2 N_T/(k_1 + k_2 N_T)$, and the factor of 2 accounts for the production of only one upconverted photon from each pair of annihilating triplets. For realistic emitters, this value can be reduced by a factor η_c, which accounts for the proportion of annihilation events that give rise to the desired singlet channel. For rubrene, we estimate this figure to be $\eta_c \simeq 0.6$,[35] while for perylene, it appears to be close to unity.[52] The quantity Φ_F is the fluorescence quantum yield of the emitter and is taken as unity. We work under the assumption that the energy of the singlet is transferred radiatively, but some cutting-edge devices use charge separation instead of radiative transfer.[46−49] At the front of the cuvette, f_2 is estimated to be just 0.0055, and thus, this device is operating far from ideal efficiency, which is where f_2 is unity.

To model the device in detail, we propagate the incoming photons into the sample from the front plane to the rear plane of the upconverter to generate a function $k_\phi(z)N_S$. From this, $W_{UC}(z)$ is calculated in a self-consistent manner, taking account of the recycling of upconverted photons due to reabsorption by the sensitizer. Reabsorption of the upconverted light by the emitter is not considered.

For the system in question, despite the inefficiencies, the calculated total current passing through the front of the sample is 2.6×10^{-3} mA cm^{-2} (assuming one electron generated per emitted photon). If the transmission of the solar cell in the spectral region of interest is as low as $T = 0.4$, as in ref 10, then the photon current emitted by the upconvertor is calculated to be just 4×10^{-4} mA cm^{-2}. When we take into account the efficiency with which the attached solar cell converts the upconverted light to current, we calculate a J_{UC} on the order of those first measured by our group (Figure 2). We draw a roadmap toward much higher efficiencies from this physically reasonable model.

Keeping the chemistry as a constant, we can optimize the optical parameters of the upconvertor. As already stated, if the transmission of the solar cell is increased to unity below its absorption threshold, the upconversion photon current density, J_{UC}, is increased to 2.6×10^{-3} mA cm^{-2}. This more than 6-fold increase reflects the quadratic response to a photon flux increase of a factor of 2.5. In addition to the transmission of the cell, the overall efficiency and absorption threshold of the cell are important to the system performance. In this Perspective, we consider devices that are optimized for upconversion efficiency, rather than the total system efficiency. As a result, the best devices for this purpose use the peak of the sun's spectral irradiance to drive upconversion, rather than the solar cell, which is always more efficient.

A thin upconverting device is cheaper and reduces reabsorption of upconverted light. As we reported previously, a back reflector for an upconvertor is crucial.[10,13] This can be in the form of a simple mirror (specular reflector) or a scattering surface (Lambertian reflector). As we have pointed out, the characteristics of the back reflector control its utility. The performance of the device outlined above is plotted as a function of the device thickness in Figure 4. The maximum calculated J_{UC} is 2.6×10^{-2} mA cm^{-2}.

The Lambertian back reflector outperforms the specular back reflector, and it is worth asking why. First, the Lambertian back reflector aids the absorption of incoming photons. Those photons not absorbed on the first pass through the sensitizer are scattered into random paths away from normal to the device surface, thus *increasing the absorption path length*. The specular mirror increases the path length by a factor of 2 because it maintains an angle of reflection that is equal to the angle of incidence. As such, the optimal device thickness is smaller for a Lambertian back reflector than the specular reflector, effectively concentrating the absorbed photons and allowing more efficient upconversion to take place. Second, the isotropic upconversion emission is also out-coupled more effectively with a Lambertian back reflector than a specular reflector. Indeed, calculations invoking a Lambertian scatterer for the incoming photons and a specular reflector for outgoing photons suggest that such a device would underperform the purely Lambertian one.

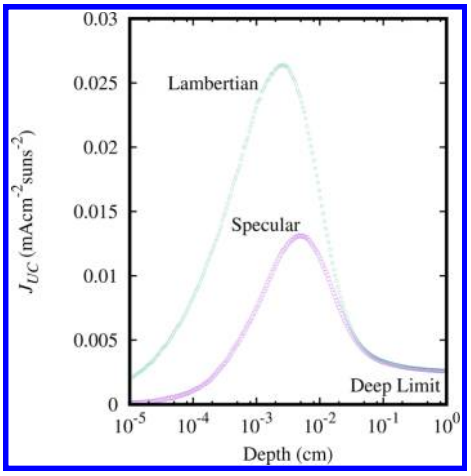

Figure 4. Simulated effect of device thickness and back-reflector properties on the upconversion current.

Engineered materials have been simulated[53−57] and tested[58−67] that outperform the essentially random Lambertian diffuser by directing upconverted light along the path with the lowest optical density to the solar cell while concentrating the electromagnetic field of the excitation light on the upconverter. A simple example is an upconverting slab on a diffraction grating,[68] excited by monochromatic light. Using a Wood's anomaly-like geometry, the excitation light is directed precisely into the plane of a thin upconverter. An enhancement factor of 10^4 has been achieved with rare earth upconverters and monochromatic excitation.[68] In this configuration, the optimal thickness of the upconverter would be greatly reduced as the optical path length of the diffracted light is very large. Bragg stack[53,54] and opal-based[58−61] upconversion devices operate under a similar principle. Plasmonic[69] upconversion devices[55−57,62−67] also concentrate electromagnetic fields but without the need for long-range order. However, they can also induce nonradiative decay.[62]

For a solar energy device, the light is not perfectly normal nor is it monochromatic. To optimize a device for optimal incoupling of sunlight and outcoupling of emission, it is helpful to model the distribution of light incidence angles. As upconversion efficiency can be nonlinear in the intensity of the light,[51] it is not sufficient to simulate an upconverter using a time-averaged distribution of light. Instead, engineered back-scatters should be optimized for a series of incidence angle distributions representing different sun positions[70] and weather patterns.[71,72] Devices based on diffraction (including Bragg stacks, photonic crystals, and opals) or plasmonics will work best if their enhancements apply to the entire absorption band of the sensitizer.

The above calculations have all been performed for a rubrene annihilator, which exhibits rather slow triplet−triplet annihilation and triplet energy transfer kinetics. There are many other annihilators, listed in Table 1, that have triplet−triplet annihilation rate constants an order of magnitude or more higher than that of rubrene. By increasing the parameter k_2 by a

Table 1. Literature Triplet–Triplet Annihilation Rate Constants[a]

molecule	phase	k_2 ($cm^3\ s^{-1}$)	ref
rubrene	crystal	7×10^{-13}	74
rubrene	solution	1.7×10^{-13}	35
anthracene	crystal	$\sim 3 \times 10^{-11}$	75–77
tetracene	crystal	1.8×10^{-11}	78
pentacene	crystal	1×10^{-10}	79
pentacene	film	$\sim 2.5 \times 10^{-11}$	79
diphenylanthracene	self-assembled in solution	3.1×10^{-11}	80
diphenylanthracene	metal–organic framework	5.5×10^{-9}	81
MEH-PPV	film	$\sim 1 \times 10^{-14}$	82

[a] Larger rate constants produce more efficient devices. The rate constant for rubrene in solution is the starting point for our calculations.

factor of 10 to 1.7×10^{-12} $cm^3\ s^{-1}$, the J_{UC} is increased to 0.18 mA cm^{-2} at a thickness of 36 μm with a Lambertian back reflector. This is significant when considering a device-relevant $J_{UC} \approx 0.1$ mA cm^{-2}. Extending this idea further to an annihilator exhibiting a 100-fold increase in k_2 compared to rubrene (e.g., 1.7×10^{-11} $cm^3\ s^{-1}$) increases J_{UC} to an impressive 0.60 mA cm^{-2} with an optimal thickness of 53 μm. This 2-orders of magnitude increase in k_2 would provide a photon upconverter with an efficiency 6-fold greater than the minimum J_{UC} for device relevance. Such ambition is a realistic target owing to the annihilation constants observed in, for example, crystalline solids.[73] To model the parameters leading to optimized upconverter performance, we set k_2 to 1.7×10^{-12} $cm^3\ s^{-1}$ as this is readily achievable in solution.

The value η_c is the efficiency with which annihilated triplet pairs produce singlet states. η_c can be reduced by resonance between the energy of two triplets and states other than a singlet. In rubrene, η_c was determined to be about 0.6,[35] which was rationalized by considering a thermally activated triplet channel. However, perylene has been demonstrated to give, in principle, singlet states with 100% efficiency upon annihilation of triplets,[52] and there is no a priori reason that an annihilator with similar spectral properties to rubrene, our example molecule, cannot also exhibit η_c approaching unity. It shall not surprise anybody that, maintaining $k_2 = 1.7 \times 10^{-12}$ $cm^3\ s^{-1}$, the J_{UC} increases by the expected ratio (1.0/0.6) to 0.30 mA cm^{-2} upon relaxing this condition.

Increasing the concentration of the sensitizer above about 1 mM in solution has not been found to be beneficial.[31,83,84] While the precise reason for this has not been elucidated, it is likely to be due to aggregation[85] or the external heavy atom effect foreshortening the lifetimes of emitter triplets. Nevertheless, should it be possible to increase N_S by a factor of 10 or more without detrimental effects, 1.04 mA cm^{-2} should be realizable at a film thickness of just 5.2 μm.

The absorption spectrum of the sensitizer is an elephant in the room.

The absorption spectrum of the sensitizer is an elephant in the room that must be addressed. All of the above calculations were performed with a single sensitizer species that uses only a small part of the available sunlight. It has been shown that multiple sensitizers can be blended to broaden the absorption spectrum of the upconvertor.[86,87] However, it is essential that the upconverter emission is still coupled out of the device. For example, if a device with a back surface consisting of fluorescent nanocrystals is used, then a large region of the spectrum can be captured by the sensitizer. This is much better than a blackbody back surface, but about half of the upconverted light will also be downconverted when it is absorbed by the back surface.

There are recent reports on the use of semiconductor nanocrystals as triplet sensitizers.[88−93] Unlike most molecular sensitizers, nanocrystals only have one transparent region in their spectrum, at low energy. However, the great utility of nanocrystals is that they allow spectral tunability with size, and therefore, they can be engineered to absorb to very low energy approaching that of the emitter triplet state. Due to the delocalization of the frontier orbitals over several nanometers, these supermolecules exhibit very small singlet–triplet gaps and can transfer absorbed photon energy to hydrocarbon acceptors bound as ligands.[89] The triplet energy has been observed to live for very long times (up to ms) on the surface of the nanocrystal, thus allowing triplet energy transfer to a potential emitter species. Indeed, upconversion from as low of an energy as 980 nm has been demonstrated using rubrene and PbSe nanocrystals.[88]

We used a published PbSe nanocrystal absorption spectrum and concentration (5.5×10^{-5} M)[88] and calibrated the nanocrystal molar extinction by extrapolating from published results.[94] We assumed excitation from 600 to 1200 nm. Our calculated device current is 0.098 mA cm^{-2} at a thickness of 240 μm. Envisioning a future solid-state device, we increased the nanocrystal concentration to 1 mM. The resulting current was 0.87 mA cm^{-2} at a thickness of 17 μm. The 290% improvement relative to PQ_4PdNA at the same sensitizer concentration is a result of the increased absorption per sensitizer.

One parameter that has not been tweaked so far is k_1, the unimolecular rate of emitter triplet state decay. Indeed, upconversion efficiency is highly sensitive to this parameter, but it was left at 1×10^4 s^{-1} in all of the above simulations. There is one report of deuteration of emitters resulting in lower k_1, effectively engineering a lower Franck–Condon factor for radiationless decay.[95] If this were able to be decreased to 1×10^3 s^{-1} for an efficient emitter that maintains an annihilation rate constant of 1.7×10^{-12} $cm^3\ s^{-1}$, then in the PQ_4PdNA/rubrene system, the J_{UC} would improve from 1.04 to 2.45 mA cm^{-2} with a thickness of 10 μm.

Even moderate solar concentration can dramatically improve the effectiveness of an upconvertor. The nanocrystal-sensitized upconvertor generating 0.87 mA cm^{-2} under 1 sun is calculated to generate 21.2 mA cm^{-2} under 10 suns at a thickness of 26 μm, a 24-fold increase, implying a doubling of efficiency, but actually a lowering of the JUC, which is penalized by the inverse square of the concentration factor. Finally, we artificially turned off reabsorption of upconverted photons to show that the reabsorption losses are 48% owing to the lack of a transparent window in the spectrum of nanocrystals.

Our simulations were benchmarked against published measurements. The sequential improvements to the upconvertor performance, which span 4 orders of magnitude, are illustrated in Figure 5. We estimate that device factors alone penalize the performance of an upconverting composition by nearly 2 orders of magnitude. The most important device factor is a properly engineered back reflector. While crude demonstrations of the efficacy of such a device have been published,[10,13] devices with high fidelity are yet to be reported.

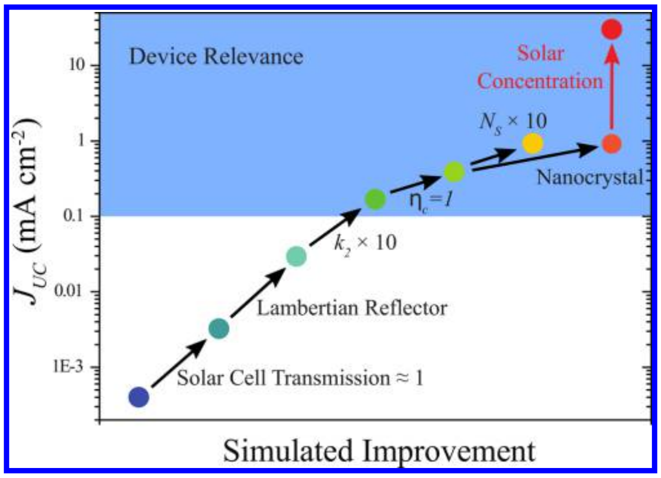

Figure 5. Improvement of the figure of merit with stepwise improvements starting from a simple deep back upconvertor. k_2: triplet−triplet annihilation constant improvement. η_c: singlet yield of annihilation improvement. N_S: sensitizer concentration.

It is best that the material in question is not a liquid but a solid.

The photochemical factors required to achieve device-relevant efficiencies, once the upconverter is properly engineered from an optical standpoint, are completely reasonable. Rubrene has been our emitter of choice until now but does not yield 100% singlets upon triplet−triplet annihilation and is also extremely slow. A system with $\eta_c \simeq 1$ and $k_2 \gtrsim 1 \times 10^{-12}$ cm^3 s^{-1} must be found. For engineering reasons, it is best that the material in question is not a liquid but a solid. While gels[96,97] have been demonstrated with identical efficiency to liquids,[98] solids are more robust. In this regard, recent reports on supramolecular upconversion assemblies[99] could be a pathway toward solid-film systems. Recent reports have shown $k_2 \approx 3 \times 10^{-11}$ cm^3 s^{-1} (Table 1) for a diphenylanthracene (DPA) derivative that self-assembled with a triplet sensitizer, even exhibiting UC emission in air.[80] The demonstration of triplet sensitization using inorganic nanocrystals from the groups of Bardeen,[88,93] Baldo,[100] and Castellano[89] could prove useful by extending thin-film deposition techniques to those not compatible with organic materials. Interestingly, Kimizuka et al. have reported a metal−organic framework (MOF) with promising upconversion efficiency in the solid state.[81] From their reported diffusion rate (D) of 2.4×10^{-3} cm^2 s^{-1}, we calculate the annihilation rate constant (k_2) to be 5.5×10^{-9} cm^3 s^{-1} based on $k_2 = 8\pi D\alpha_0$, where α_0 is the annihilation distance between emitter triplets (9.1 Å for DPA triplets[101]). This strikingly large k_2 prediction suggests that we are on the cusp of a paradigm shift, whereby condensed-phase upconversion is not limited by molecular diffusion. Taken together, these form a concerted drive toward the development of efficient PUC materials in the condensed phase.

This is not without its challenges, and it is worth noting that one pitfall of the solid state is the presence of trap states.[73] Numerous strategies have been employed toward engineering the microscopic morphology of thin films to circumvent trap sites that limit the overall efficiency. Common approaches involve dispersion of the sensitizer and emitter components in an electronically inert polymer matrix to form a rubber/glass/solid solution.[96,102−108] To date, these systems have exhibited poor overall efficiency compared to their solution-phase equivalents, with poor triplet exciton mobility through the matrix causing a detrimental loss in the efficiencies of energy transfer and annihilation events.[109]

An extension of a polymer matrix-based thin-film device is to use the polymer as a electronically relevant component in the PUC active layer. The combination of π-conjugated semiconducting polymers with porphyrin-based sensitizers has been employed to produce upconverted photons through emission from the polymer phases.[110−114] These systems have good triplet mobility and are amenable to thin films. However, these π-conjugated-based systems suffer overall PUC efficiencies lagging behind those of solution and even other condensed-phase systems. Furthermore, there appears to be a lack of recent literature showing improvements, suggesting efficiency gains on this approach could be stalling. The limit on photon upconversion efficiency in π-conjugated polymer-based PUC systems appears to result from two factors: (1) phase separation of the sensitizer and π-conjugated polymer leading to trap state losses and (2) inherently low k_2 values of commonly employed π-conjugated polymers, with the annihilation rate constant of MEH-PPV (Table 1),[82] for example, being almost an order of magnitude lower than that of rubrene in solution.[35] On the basis of our calculations, this is two orders of magnitude lower than required to achieve a device-relevant upconversion photon current density (J_{UC}). The pathway forward must involve the design of π-conjugated materials addressing these factors. Our modeling provides motivational target values for photochemical parameters.

Concentration of the sensitizer material is also a crucial factor. A 10-fold increase in the concentration of the sensitizer could, in principle, give rise to a 10-fold increase in the J_{UC} at low efficiency. Whether this could be achieved is another matter, but there is hope. Not all sensitizers need bear a heavy metal atom,[115,116] and if this is the cause of the detrimental effects at high concentration, then this factor can be mitigated by the use of metal-free sensitizers such as the compounds utilized in thermally activated delayed fluorescence (E-type delayed fluorescence) in organic light-emitting diodes.[117] These molecules have spatially separated highest-occupied and lowest-unoccupied molecular orbitals, which diminishes the exchange integral and brings the S$_1$ and T$_1$ states together energetically. Sensitizer absorption can also be enhanced by plasmon resonance.[55−57,62−67]

Future devices will far exceed the threshold for device relevance.

We have proposed a framework for increasing the efficiency of PUC toward device relevance. While experimental upconversion results so far do not contribute a meaningful amount to solar energy conversion, our calculations show that, under reasonable assumptions, future devices will far exceed the threshold for device relevance. In our view, the real experimental challenges are (1) optimizing device thickness, (20) maintaining a high k_2 when other parameters are optimized, and (3) avoiding phase segregation of sensitizers.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: timothy.schmidt@unsw.edu.au.

ORCID

T. W. Schmidt: 0000-0001-6691-1438

Notes

The authors declare no competing financial interest.

Biographies

Laszlo Frazer is a Research Associate in the School of Chemistry and ARC Centre of Excellence in Exciton Science at The University of New South Wales. The emphasis of his work is on exciton scattering, with a particular focus on efficient energy capture.

Joseph K. Gallaher is a Research Associate in the ARC Centre of Excellence in Exciton Science at The University of New South Wales, Australia. His research interests lie in the synthesis, photophysics, and applications of optoelectronic devices, particularly the development of new technologies to better capture the sun's power as a renewable energy resource.

Timothy W. Schmidt is a Professor of Chemistry at The University of New South Wales, in Sydney, Australia, and a chief investigator in the ARC Centre of Excellence in Exciton Science. His research group studies molecular spectroscopy, both in the condensed and gas phases, with applications ranging from astrophysics to renewable energy.

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