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Dye-Sensitized Solar Cell with Integrated Triplet–Triplet Annihilation Upconversion System

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S *Supporting Information*

ABSTRACT: Photon upconversion (UC) by triplet–triplet annihilation (TTA-UC) is employed in order to enhance the response of solar cells to sub-bandgap light. Here, we present the first report of an integrated photovoltaic device, combining a dye-sensitized solar cell (DSC) and TTA-UC system. The integrated device displays enhanced current under sub-bandgap illumination, resulting in a figure of merit (FoM) under low concentration (3 suns), which is competitive with the best values recorded to date for nonintegrated systems. Thus, we demonstrate both the compatibility of DSC and TTA-UC and a viable method for device integration.
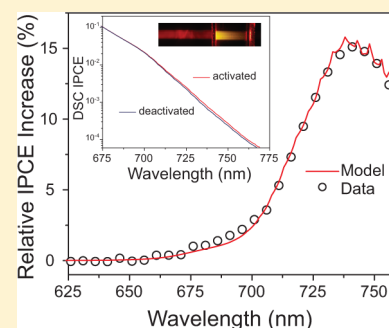
SECTION: Energy Conversion and Storage; Energy and Charge Transport

D ye-sensitized solar cells (DSCs) make up a photovoltaic technology that has generated significant interest across a broad range of research fields[1] since their first report.[2] In spite of this wealth of research, the highest reported device efficiencies, to date, remain relatively low. However, this is arguably compensated by low projected manufacturing costs[3] and their strong performance in ambient and diffuse lighting conditions.

The large driving forces required for effective charge transfer in DSCs[4] necessitate the use of absorbers with large absorption thresholds. This has been seen for both working high-efficiency devices[5] and in theoretical optimization calculations.[6,7] This large energy gap results in a significant section of the solar spectrum remaining unutilized by the cell.

One approach to utilize this sub-bandgap light is to incorporate a photon upconversion (UC) system, which pools the energies of two long wavelength photons to emit a single higher energy photon that can be better absorbed by the active layer of the solar cell. Because this process allows for the utilization of photons with energy less than the bandgap, UC-assisted solar cells have a higher efficiency limit than single junction devices (Shockley–Queisser limit[8,9]) and are an example of a third-generation PV technology.[10]

Various research groups have applied UC systems to a number of different types of solar cells, including gallium arsenide (GaAs),[11] crystalline silicon (c-Si),[12–14] amorphous silicon (a-Si)[15,16] and organic (OPV) solar cells,[17] with the aim

of enhanced current generation from near- or sub-bandgap energy photons. A number of groups have applied UC systems to DSCs.[18–20] However, in all of these examples, the source of UC has been sequential energy transfers (SET) based on rare-earth metal ions.[21] Rare-earth ion-based UC is a process that involves transitions between 4*f* orbitals. These transitions are Laporte forbidden, indicating the fundamentally weak excitation of rare-earth ion-based UC,[22] and making this process poorly suited to the lighting conditions (low intensity, incoherent) under which DSCs excel. Moreover, the atomic nature of rare-earth absorbers gives them narrow absorption bands. Nevertheless, Hummelen and co-workers recently demonstrated an approach to broaden the absorption range of rare-earth upconvertors by sensitizing the rare-earth metal ions with dyes.[23]

Upconversion based on triplet–triplet annihilation (TTA-UC, shown schematically in Scheme 1) occurs in molecular species, which have broader and significantly stronger electronic transitions than rare-earth metals. Therefore, TTA-UC is a viable route to high UC efficiencies at lower light intensities[25–30] compared to rare-earth based UC.[21]
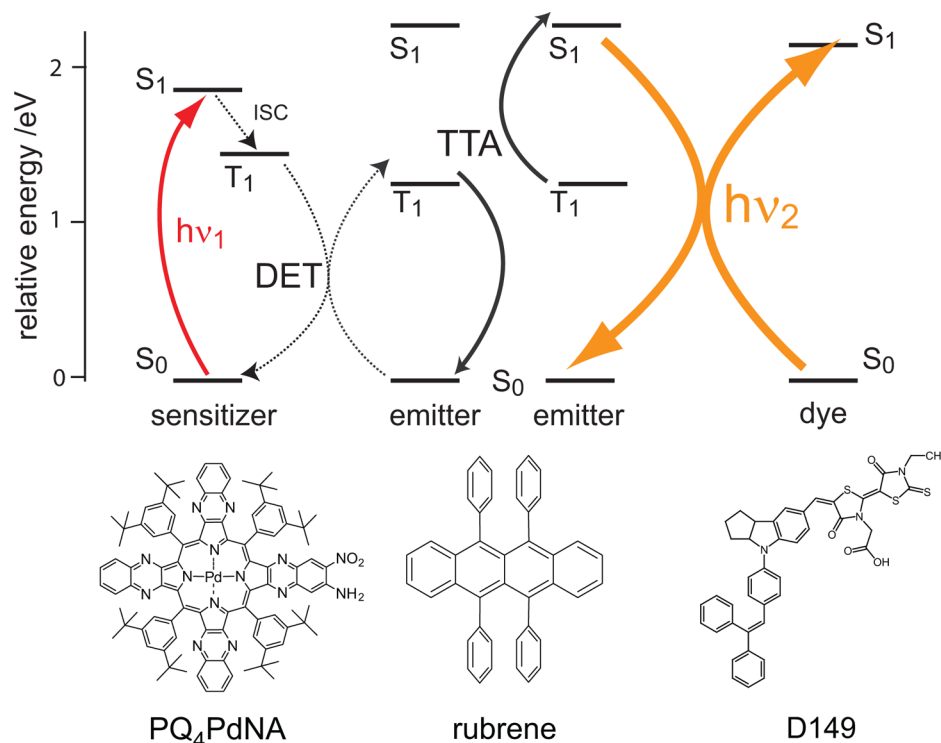
Previously we have shown that TTA-UC can improve the sub-bandgap sensitivity of a-Si[31–33] and OPV[34] cells, and

Scheme 1. Schematic Representation of Triplet−Triplet Annihilation-Based Upconversion[a]

[a]A ground-state PQ$_4$PdNA sensitizer molecule absorbs a low energy photon (hν_1), then undergoes intersystem crossing (ISC) to the first triplet state. The energy from this triplet is then transferred via a Dexter energy transfer (DET) process[24] to a ground state rubrene emitter molecule, which is transferred to a triplet state. TTA occurs between two such excited emitters via a collisional complex to yield one emitter in the first singlet excited state and the other in the ground state. The excited singlet emitter returns to the ground state via emission of a higher energy upconverted photon (hν_2), which is captured by the D149 dye in the present case.

Castellano's group has observed the activation of WO$_3$ photoanodes under incoherent sub-bandgap excitation with the assistance of a TTA-UC system.[35] However, the UC systems in those works were in the form of a solution held in a cuvette. Herein we present an integrated device, demonstrating a practical method for incorporating TTA-UC into DSC (as well as other PV devices). The solution-based UC system is contained within an encapsulated chamber, similar to that which holds the active DSC system. This chamber can be engineered to have a thickness that allows optimal output from the TTA-UC solution, in accordance with our previous study.[32,33] Using benzene as the solvent, we were able to increase the concentration of UC components compared to using toluene, thereby decreasing the optimal thickness to ~120 μm. This architecture bears resemblance to previously reported tandem DSC architectures.[36,37] However, no extra TCO layer is required because the second cavity uses plain soda lime glass resulting in minimal additional cost. Furthermore, the dependence on current/voltage matching (Kirchoff's laws) is not an issue as it is for multijunction photovoltaics.[38,39,50]

The TTA-UC system used in this work (PQ$_4$PdNA + Rubrene, Scheme 1) was previously shown to enhance a-Si and OPV performance.[31,32,34] The sensitizer has strong absorptions in the 670 nm region ($\varepsilon \sim 6 \times 10^4$ M^{-1} cm^{-1}) and phosphorescence ($\tau \sim 100$ μs) in the 890 nm region, which is effectively quenched by the 33 mM rubrene used here. Rubrene has a triplet lifetime under the employed conditions of 110 μs, and a triplet−triplet annihilation rate constant of ~10^8 M^{-1} s^{-1}.[25] The peak emission wavelength of rubrene complements a

number of dyes used in high efficiency DSCs, including D149,[40,41] which was used in this study.

TTA-UC is a nonlinear process under low intensity excitation due to the bimolecular nature of the effect.[42−44] This study was therefore carried out with background excitation by a 670 nm laser diode (the pump beam), and we probed the device response with a weak, chopped monochromated light source (the probe beam). The pump beam acted to increase the background concentration of triplet states, making the system more responsive to the probe beam when the two beams were aligned on the sample. Baseline measurements of the cell response were made with the two beams misaligned, thereby rendering the UC unresponsive to the low intensity probe beam. The ratio of the aligned and misaligned measurements yielded a measure of the improvement in cell performance due to UC. Enhanced response to light in the region 600−750 nm was observed using pump beam intensity as low as ~3 equivalent suns (☉). For clarity, 3☉ means the excitation rate of the sensitizer at the center of the Gaussian pump beam is 3 times the rate under exposure to the portion of AM1.5G in the region of the sensitizer Q-band absorption (600−770 nm, filtered by the solar cell, Figure S2d). The relative peak enhancement was improved by further increasing pump intensity (and thus the background triplet population in the probed region).

Figure 1 shows this relative enhancement for a relatively high pump intensity (results of other intensities are shown in the Supporting Information). Importantly, the shape of the incident photon to charge carrier conversion efficiency (IPCE) gain curve (Figure 1 insert) very closely follows the
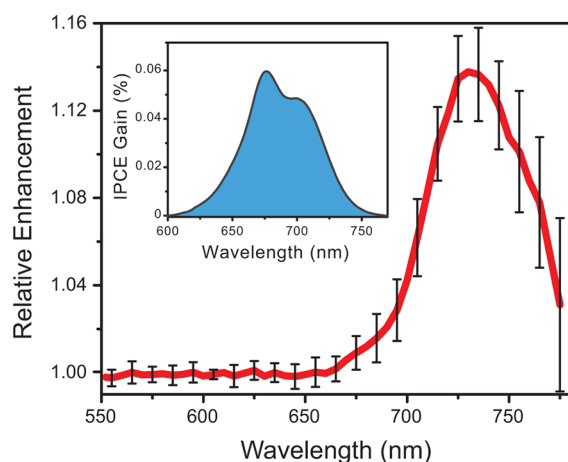
Figure 1. Relative peak enhancement trace for a device tested with ~24 suns equivalent illumination (λ = 670 ± 5 nm), with insert showing the gain in IPCE, attributable to the TTA-UC system. The error bars indicate variability over multiple measurements on the same cell.

product of the PQ$_4$PdNA absorption spectrum and the device transmission (Figure S2), clearly indicating the source of the enhanced performance to be TTA-UC. The relative enhancement of the IPCE was measured at a range of light intensities, and was integrated over the AM1.5G spectrum to predict the expected increase in short circuit current density (ΔJ_{SC}) under solar irradiation. For comparing to results obtained from other TTA-UC assisted solar cells, we normalize ΔJ_{SC}'s by the square of the corresponding solar concentration factor, since TTA-UC is a quadratic process at low intensities. The resulting (conservative) figure of merit (FoM) has previously been demonstrated to be valid in the low excitation intensity regime.[34] Using the FoM allows for a relatively straightforward extrapolation to the expected enhancement of device performance under ambient light conditions (1$\odot$) due to TTA-UC.

Figure 2 shows measurable improvements in device performance at all light intensities measured, down to ~3$\odot$ equivalent. Results are displayed as both ΔJ_{SC} and FoM.

It was initially expected that the FoM would be constant at lower light intensities. In the present work, FoM was found to decrease with increasing excitation power (Figure 2b), indicating saturation of the TTA-UC system efficiency under our chosen excitation conditions. From the dual logarithmic plot of ΔJ_{SC} as a function of effective solar concentration (Figure 2a), we observe a change in slope from nearly 2 to approaching 1 with increasing concentration factor. This shows that the TTA-UC system operated within a subquadratic regime, and almost reached the linear regime in which TTA-UC efficiency is maximized[42] under pump illumination equivalent to 24.4$\odot$. In the subquadratic regime, the output of upconverted photons (and thus ΔJ_{SC}) does not increase quadratically with increasing excitation power, and therefore the FoM drops.

As mentioned, it was anticipated that the FoM would plateau at low excitation powers. However, from Figure 2b, it is clear that the FoM does not reach such a plateau at the minimum pump intensity used here. This was due, in part, to difficulties measuring enhancement effects when the power of the pump beam approached that of the probe, resulting in low contrast between the aligned and misaligned measurements (Figure S1(a)) and a poor signal-to-background ratio. The probe was estimated to be equivalent to ~0.3$\odot$, and a pump of 3$\odot$ was the lowest at which an enhancement significantly greater than the system noise was obtained. Even at low excitation power, the TTA-UC system appears to operate in the subquadratic regime. This indicates that our measurement system requires a contrast of 1:100 (0.09$\odot^2$ to 9$\odot^2$) for data acquisition. There is a need to improve the sensitivity of this system to acquire data that can demonstrate a plateau in FoM and thus uncover the maximum FoM of integrated devices.

Under 3$\odot$ equivalent excitation, an FoM of 2.5 × 10^{-4} mA cm^{-2} was obtained, which exceeds the FoMs obtained for P3HT:ICBA and PCDTBT:PC$_{71}$PM organic solar cells, but is still less than the FoMs achieved for (n)a-Si:H/(i)a-Si:H/(p)μc-SiO$_x$:H.[34] This is due, in part, to measurement issues arising from the unique structure of the DSC, and the differing efficiencies of the a-Si:H and DSC cells. Additionally, the large gap (4 mm) between the active DSC layer and the TTA-UC
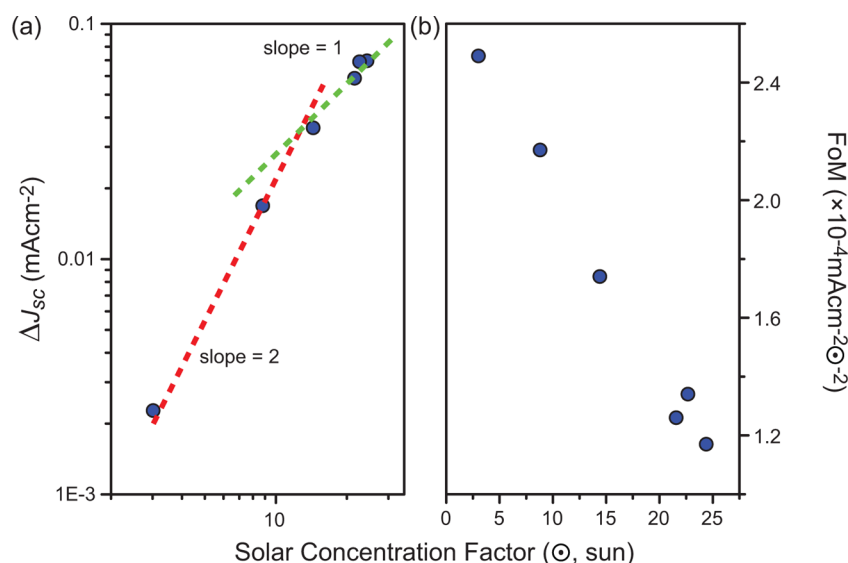

Figure 2. (a) Dependence of calculated current gain (ΔJ_{SC}) on effective solar concentration (both axes on a logarithmic scale). (b) FoM as a function of solar concentration.

medium and the location of upconversion limited the amount of upconverted light reaching the active layer (shown schematically in Figure S1b). This shortcoming will be addressed in future integrated devices.

According to a previous study of TTA-UC kinetics, we can estimate the portion of triplets consumed through TTA (f_2) under continuous illumination,[25]

$$f_2 = \frac{k_2[^3M^*]}{k_1 + k_2[^3M^*]} \qquad (1)$$

where k_2 is the rubrene TTA rate, k_1 is the rubrene triplet decay rate and $[^3M^*]$ is the rubrene triplet concentration. Under steady-state conditions, the rate of generation and consumption of triplets are equal, thus $[^3M^*]$ can be calculated:

$$ck_\phi[^1M] = k_1[^3M^*] + k_2[^3M^*]^2 \qquad (2)$$

where c is the solar concentration factor, k_ϕ is the excitation rate of PQ$_4$PdNA under 1 sun (derivation supplied in the Supporting Information) and $[^1M]$ is the concentration of PQ$_4$PdNA. k_1 of the rubrene triplet in benzene has been reported to be $\sim$8900 s^{-1},[45] k_2 of rubrene was estimated to be $\sim$1.0 $\times$ 10^8 M^{-1}s^{-1} in our previous kinetics study,[25] and k_ϕ is 3.6 s^{-1} under the conditions of this study (see Supporting Information). Using eqs 1 and 2 with the stated parameters and under 24$\odot$ excitation, f_2 is 5.8%. This indicates inefficient utilization of triplets generated from transmitted low energy photons. As a consequence, the ΔJ_{SC} and FoM values reported here likely underestimate the true device potential to a significant degree. Moreover benzene, the solvent we used for TTA-UC mixture, deteriorates the seal around the TTA-UC chamber, limiting device longevity. The results presented are for our best example. Ionic liquid[46] or polyhedral oligomeric silsesquioxane[47] are possible alternative media for TTA-UC, and solid state upconvertors have also been reported.[48,49] Efforts are underway to improve the low light intensity performance of the TTA-UC system in order to realize the possibilities of this integrated DSC-TTA-UC architecture.

The devices described above are the first report in which a TTA-UC system has been fully integrated into a photovoltaic device, and also represent the first time TTA-UC has been reported to enhance the performance of a DSC.

The FoM values obtained for this integrated device are competitive with the best observed thus far. Efforts to further improve this performance are underway. In addition, efforts are being made to improve the characterization technique such that lower light intensity measurements can be made more reliably.
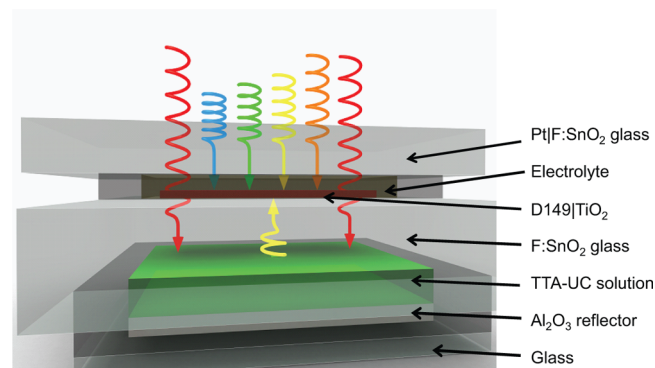
■ EXPERIMENTAL SECTION

DSC Preparation. The photoanode was created atop a sheet of F:SnO$_2$ glass (4 mm, 7 Ω/□, Nippon Sheet Glass) as described in a previous report.[50] A dense layer of TiO$_2$ was deposited using a spray pyrolysis technique,[51] followed by screen printing of a 3 μm mesoporous TiO$_2$ layer (Dyesol 18NR-T), which was sintered then treated with TiCl$_4$. After a further sintering step, the films were dyed with D149[40] (structure shown in Scheme 1, 0.5 mM in a 1:1 mixture of MeCN:tBuOH) for 2 h.

The counter electrode was produced by thermal decomposition of H$_2$PtCl$_6$, deposited from a 10 mM ethanolic solution, spread across another sheet of F:SnO$_2$ glass (3 mm, 8 Ω/□, Nippon Sheet Glass) with a pipet tip to ensure thin, homogeneous coverage. After thermal decomposition at 400 °C the electrode transparency in the wavelength range 600−800

nm was diminished by only $\sim$2.5% due to this Pt layer. Devices comprised of the photoanode and catalytic cathode described above were assembled using Surlyn (25 μm, Solaronix SA) hot melt adhesive. The back cavity was created using a piece of glass coated with a $\sim$10 μm layer of Al$_2$O$_3$ as a scattering reflector (doctor bladed from a paste comprised of 2 g of 300 nm particles from Leco, 4 mL of a 50 nm Alfa Aesar colloidal dispersion and 2 mL ethanol). This was pressed onto the back of the working electrode glass using two sheets of 60 μm Surlyn, as shown in Scheme 2, with the rationale for using a 120

Scheme 2. A Schematic Showing the Structure of the Integrated Device[a]

Pt|F:SnO$_2$ glass
Electrolyte
D149|TiO$_2$
F:SnO$_2$ glass
TTA-UC solution
Al$_2$O$_3$ reflector
Glass

[a]Low-energy photons pass through the active layer of the device and cause TTA-UC in the TTA-UC layer. Upconverted photons that are absorbed by the active layer provide extra current to the device.

μm TTA-UC chamber explained below. The front chamber of the device was filled with an electrolyte containing 50 mM iodine (Sigma), 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (Solaronix), and 0.1 M lithium iodide (Sigma) in methoxypropionitrile (Sigma) using a backfilling technique, before being sealed with aluminum-backed Surlyn. At this point, devices were transferred into a glovebox.

TTA-UC Solution Preparation and Inclusion into Device. The TTA-UC solution was prepared by dissolving {5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)-6′-amino-7′-nitro-tetrakisquinoxalino[2,3-*b*′7,8-*b*″12,13-*b*‴17,18-*b*‴′]-porphyrinato} palladium(II) (PQ$_4$PdNA, synthesized in the School of Chemistry, the University of Sydney[52]) along with rubrene (Sigma-Aldrich (>98%)) in dry benzene (structures shown in Scheme 1) to a concentration of 0.6 mM and 33 mM, respectively. Benzene was used instead of toluene, unlike previous studies,[31,32,34] to increase the solubility of rubrene (e.g., 39 mM in benzene at 20 °C[53] and $\sim$22 mM in toluene at 40 °C[54]). With this concentration of PQ$_4$PdNA and a molar extinction coefficient of about 58000 M^{-1}cm^{-1}, the light at peak absorbance of the PQ$_4$PdNA will attenuate to $1/e^2$ of its original intensity after propagating twice through the 120 μm TTA-UC medium.[32] The TTA-UC solution was deaerated thoroughly by three freeze−pump−thaw cycles ($\sim$10^{-4} mbar) while maintaining minimal exposure to light. The TTA-UC solution was introduced into the back cavity of the device using two holes and allowing capillary forces to draw the solution through. These holes were then sealed, again using aluminum-backed Surlyn.

Enhancement Determination. Devices were removed from the glovebox and tested in a similar manner to previous reports.[31,32,34] Since the yield from TTA-UC has been shown

to scale nonlinearly at low excitation densities, we can activate the TTA-UC mixture by generating a background population of triplets with a pump beam, a 670 nm continuous wave red diode laser (which matches the peak absorption wavelength of PQ$_4$PdNA), and probe the spectral response of the cell plus TTA-UC system using another weak chopped light source. The mW pump beam was approximately Gaussian in shape, with a $1/e^2$ area of ~0.8 mm^2. The probe beam was smaller, and aligned with the most intense part. The pumping rate at the center was matched with an equivalent (filtered) solar concentration, which was maximally determined to be 24⊙.

The yield of upconverted photons from the probe alone (when the pump and probe beam are misaligned) is negligible. Due to the quadratic behavior of the TTA-UC system at low excitation power, upconversion intensity corresponding to the probe (0.3⊙) itself is estimated to be 1% of that under the lowest power laser bias (3⊙). We determined the enhancement in IPCE of a D149 cell responding to TTA-UC by scanning the probe light through the visible spectrum (500−780 nm) with the pump and probe beam aligned and then misaligned. As such, the DSC was subjected to approximately the same background illumination conditions for the two scans. For detailed information regarding measurements and FoM calculation, please refer to the Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Relative enhancement measurement details, FoM determination, D149 cell transmittance and ICPE, absorption of PQ$_4$PdNA, emission spectra of rubrene, and relative IPCE enhancement under various excitation intensities. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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