

Getting to the (Square) Root of the Problem: How to Make Noncoherent Pumped Upconversion Linear

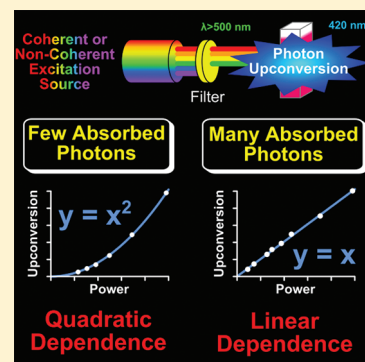
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S Supporting Information

ABSTRACT: We present experimental data illustrating that photochemical upconversion based on sensitized triplet–triplet annihilation can exhibit anti-Stokes emissions whose intensities with respect to the excitation power can vary between quadratic and linear using a noncoherent polychromatic light source. The benchmark upconverting composition consisting of Pd(II) octaethylporphyrin (PdOEP) sensitizers and 9,10-diphenylanthracene (DPA) acceptors/annihilators in toluene was selected to generate quadratic, intermediate, and linear behavior under both coherent and noncoherent excitation conditions. Each of these power laws was traversed in a single sample in one contiguous experiment through selective pumping of the sensitizer using an Ar⁺ laser. Wavelength-dependent responses ranging from quadratic to pseudolinear were also recorded from the identical sample composition when excited by Xe lamp/monochromator output in a conventional fluorimeter, where the optical density at λ_{ex} dictates the observed incident power dependence. Finally, pure linear behavior was derived from noncoherent excitation for the first time at higher sensitizer concentrations.

SECTION: Kinetics, Spectroscopy



Sensitized triplet–triplet annihilation (TTA) or sensitized triplet fusion is a regenerative photochemical process resulting in the frequency upconversion of light.¹ This technology appears to be well poised to assist photovoltaics in exceeding the Shockley–Queisser limit² by enabling the capture and conversion of sub-bandgap light, thereby artificially creating an improved spectral match to the solar spectrum. In general terms, photochemical upconversion is facilitated by selective excitation of sensitizer chromophores that intersystem cross to the long-lived lowest energy triplet excited state with high quantum efficiency. Dexter-type triplet–triplet energy transfer then occurs to molecular acceptor species energetically poised for TTA and, thus, the desired annihilation-producing anti-Stokes fluorescence. In the majority of recent cases, late transition-metal-based sensitizers are used in tandem with a variety of organic-based triplet acceptors/annihilators in fluid solution,^{3–15} and the upconverted photons are easily visualized by the naked eye, unless bond forming chemistry is desired.¹⁶ These sequential bimolecular reactions have also been translated into soft and hard polymer host matrices,^{17–21} a critical prerequisite for device integration. Fortunately, the quantum efficiency of triplet fusion is not limited by spin statistics, since the quintet and triplet dimers likely recycle excited triplets,^{1,12–14} and has been estimated to have an upper limit exceeding 40%.^{12–14} In laboratory experiments, measured sensitized TTA quantum efficiencies have already exceeded the so-called 11% spin statistical limit,^{1,3,12–14} implying that device integration may be on the horizon.²²

A convenient metric typically employed to mechanistically support sensitized photochemical upconversion through TTA is the quadratic incident light power dependence exhibited by the anti-Stokes fluorescence, as first described by Parker and Hatchard.²³ This power dependence is typically evaluated in steady-state photoluminescence experiments using a variety of either coherent (laser) or noncoherent (lamp) excitation sources that can vary in irradiance over many orders of magnitude. However, recent experiments utilizing either continuous-wave or high peak power-pulsed ultrafast lasers have illustrated that a linear power law can also be achieved in Pt(II) octaethylporphyrin (PtOEP)/9,10-diphenylanthracene (DPA) and PQ₄Pd/rubrene solution-based TTA compositions, respectively, at higher light intensities.^{12,14,24} Importantly, in this latter regime, the upconverted emission intensity is directly proportional to the number of triplet excited states sensitized, meaning that the highest possible quantum efficiency for the specific composition has been realized.^{14,24} Although sensitized TTA is inherently a noncoherent process, only a handful of studies have achieved detectable photon upconversion in the absence of laser excitation,^{6–8,18} and none of these investigations have quantitatively demonstrated the realization of the desirable high quantum efficiency linear power regime using noncoherent photons.

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Interested in driving sensitized triplet fusion processes at their highest possible efficiency using noncoherent solar photons, we experimentally demonstrate for the first time incident light power dependence ranging between quadratic and linear in photochemical upconversion from the prototypical Pd(II) octaethylporphyrin (PdOEP)/DPA composition^{1,6,18} in toluene solutions using appropriately filtered lamp excitation. Importantly, the high quantum efficiency linear regime is achieved with noncoherent pumping of the PdOEP sensitizer at incident light power levels provided by the sun (AM 1.5G) integrated across the low energy Q-bands of the sensitizer. To facilitate comparisons to previous related work accomplished with a coherent light source,²⁴ we also produced clear-cut quadratic, intermediate, and linear power laws in a similar composition using an Ar⁺ laser, $\lambda_{\text{ex}} = 514.5$ nm.

The chemical structures of the PdOEP sensitizer and DPA acceptor/annihilator used in this study along with their normalized ground state absorption and emission spectra measured in toluene are presented in Figure 1. PdOEP, whose phosphorescence is

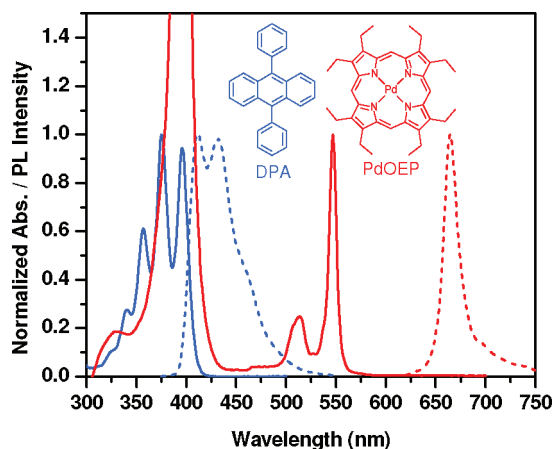


Figure 1. Absorption (solid lines) and photoluminescence (dashed lines) spectra of the independent PdOEP (red) and DPA (blue) chromophores in toluene.

centered at 665 nm in deaerated toluene, exhibits characteristic absorptions at 400 nm (Soret) in the blue along with two Q-band features at lower energy in the green ($\lambda_{\text{max}} = 513$ nm, 545 nm).

These latter features are well separated from the lowest energy DPA $\pi-\pi^*$ absorption bands, ensuring that Q-band excitation results exclusively in sensitizer excitation. In toluene, dynamic quenching of PdOEP by DPA through a triplet–triplet energy transfer rate constant is significant ($1.4 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) with a corresponding Stern–Volmer constant of $123\,000 \text{ M}^{-1}$ (Figure S3, Supporting Information). Unless otherwise stated, all upconversion experiments utilize a mixture of PdOEP (5 μM) and DPA (100 μM) in toluene, ensuring that the absorbed photons are converted into sensitized triplets so rapidly that the excited state triplet concentration, $[^3A^*]$, linearly scales with excitation power. The power density imposed on each sample was systematically varied using neutral density filters, each measured with a power meter.

Figure 2a presents the double logarithm plot generated using the intensity of the singlet fluorescence emanating from DPA at 420 ± 6 nm measured as a function of incident power density over several decades when PdOEP is selectively excited using the bandpass filtered 514.5 nm output from an Ar⁺ laser in argon-saturated toluene. We were able to achieve such a wide dynamic range in photon counting detection sensitivity by using various combinations of neutral density filters in the emission path when mandated, later correcting the raw data for the light absorbed by the filter(s). As anticipated, at low incident powers, the slope of this plot is 2.0, indicative of quadratic dependence (also see Figure S5). Upon increasing the photon flux incident on the sample, the plot deviates off this initial slope, a process that perpetuates until the sample ultimately achieves a slope of 1.0 at the highest incident power densities (also see Figure S6). This result clearly demonstrates that in a single sample, a variety of power-dependent responses can be measured depending upon the initial and final photon flux utilized in the experiment and is analogous to that observed in related investigations on different sensitized TTA compositions.^{14,24} Figure 2b displays the same data plotted on linear x – y axes to illustrate the significant gain in upconversion quantum efficiency once the threshold to the linear regime is achieved.²⁴

Noncoherent excitation was then applied to samples identical to those above, now vacuum degassed, at select wavelengths spanning the low energy Q-band region of PdOEP. Three freeze–pump–thaw cycles with a vacuum of 8–10 μm essentially removes all residual dissolved O₂, resulting in the

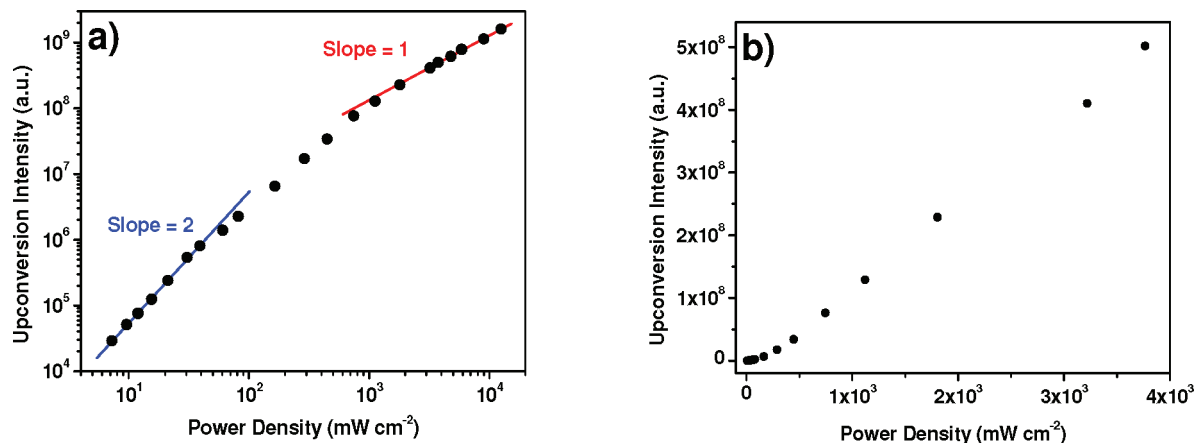


Figure 2. (a) Double logarithmic plot of the upconversion emission signal at 420 ± 6 nm measured as a function of 514.5 nm incident laser power in a mixture of PdOEP (5 μM , O.D. @ 515 nm = 0.08) and DPA (0.1 mM) in argon-degassed toluene. The colored lines are the linear fits with slopes of 1.0 (red, linear response) and 2.0 (blue, quadratic response) in the high and low power regimes, respectively. (b) Linear plot of the first 19 data points presented in panel a.

elimination of its pseudo-first-order quenching of the formed acceptor/annihilator triplets; the sample is then poised to more efficiently facilitate second-order annihilation chemistry, as suggested by kinetic simulations.¹⁴ In these conventional fluorimeter-based experiments, the 450 W Xe lamp output was passed through a monochromator to tune the excitation followed by a 455 nm long pass filter to remove any extraneous high-energy components. These experimental conditions readily permit evaluation of how sensitizer optical density affects the resultant incident power dependence, conveniently measured as a function of excitation wavelength in the same sample. Higher optical densities promote larger light absorption and sensitized triplet formation, thereby simulating an environment exposed to higher light fluence. Identical to the analysis provided above in Figure 2a, Figure 3 presents some of the associated double

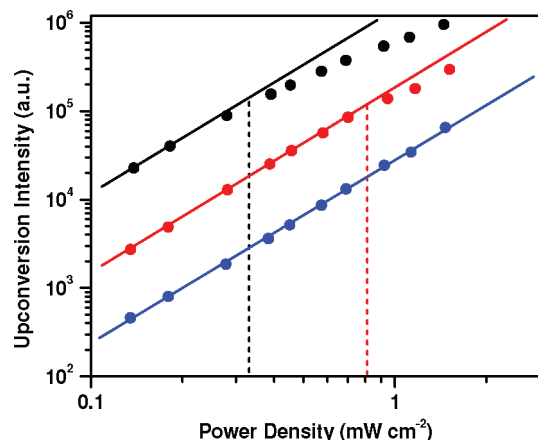


Figure 3. Upconversion emission signal at 420 ± 6 nm measured as a function of three distinct noncoherent excitation wavelengths (± 10 nm) in a mixture of PdOEP (5 μ M) and DPA (0.1 mM) in vacuum-degassed toluene. The solid lines represent the quadratic power dependence fits (slope = 2.0) at three excitation wavelengths: 545 (black), 515 (red), and 530 nm (blue). The dashed lines indicate the approximate position where deviation away from quadratic behavior occurs at each Q-band maximum: 515 nm (O.D. = 0.08) and 545 nm (O.D. = 0.29), respectively.

logarithmic responses to noncoherent excitation power measured at three distinct wavelengths across the Q-band region of the PdOEP sensitizer: $\lambda_{\text{ex}} = 515$, 530, and 545 nm. In these investigations, findings similar to those described above are readily apparent, except that deviations from pure quadratic behavior now occur at rather low excitation power since we significantly decreased the first-order component in $^3A^*$ decay in these vacuum degassed samples. The graphical position where the slope deviates from quadratic (dashed lines) depends largely on the optical density at λ_{ex} . This is completely expected given that the specific power law response is dictated by the amount of light absorbed in the sample. In fact, a fit of the last five data points at 545 nm in Figure 3 produces a slope of 1.3, so even this conservative experiment approaches linear behavior at higher incident power densities. The ultimate conclusion here is that noncoherent light sources also induce significant deviations from quadratic behavior in photochemical upconversion, and wavelength-dependent power laws can be readily achieved at various excitation intensities. These are important points to consider when evaluating new compositions in future investigations.

Finally, the question remained as to whether photochemical upconversion could achieve completely linear incident light

power dependence when pumped by noncoherent photons. Given the data presented in Figure 3, we decided to increase the sensitizer concentration to provide an O.D. of 1.9 in the Q-band maximum at 545 nm and measure the resultant upconverted DPA emission (420 ± 4 nm) in front-face geometry in the spectrofluorimeter. The results of these experiments are presented in Figure 4, once again plotted as a double logarithm

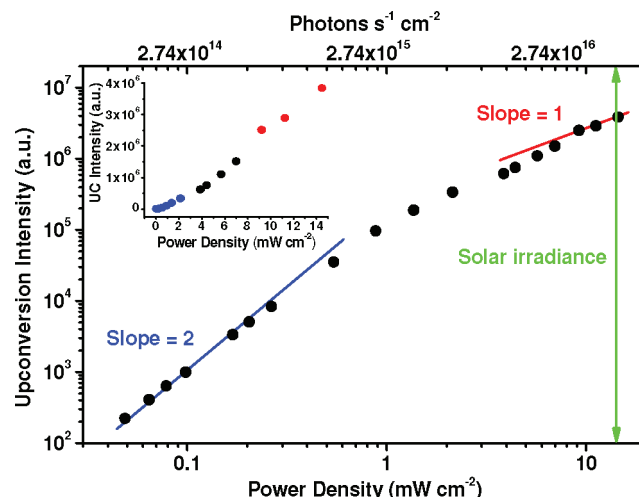


Figure 4. Double logarithmic plot of the upconversion emission signal at 420 ± 4 nm measured as a function of 545 ± 10 nm incident noncoherent photons in a mixture of PdOEP (38 μ M, O.D. @ 545 nm = 1.9) and DPA (0.78 mM) in vacuum-degassed toluene. The solid lines are the linear fits with slopes of 1.0 (red, linear response) and 2.0 (blue, quadratic response) in the high and low power regimes, respectively. The green vertical line indicates the one-sun solar irradiance (AM 1.5) integrated across the Q-band absorption profile of PdOEP (475–575 nm). Inset: linear plot of the same data coded as blue (quadratic), black (intermediate), and red (linear), illustrating the relative yields of the various incident light power dependencies.

response. From below $100 \mu\text{W cm}^{-2}$ to approximately 1 mW cm^{-2} incident power density using 545 ± 10 nm Xe lamp excitation, the power law exhibited by the composition was clearly quadratic. Deviations away from this “square” behavior occurred at $\sim 2 \text{ mW cm}^{-2}$ and continued to flatten toward a pure linear response, which was finally achieved at 10 mW cm^{-2} . The Figure 4 inset presents the same data plotted on linear x – y scales, illustrating the substantial gain in upconversion yield upon reaching the linear regime.²⁴ Unfortunately, the maximum light fluence that we could obtain in our fluorimeter was only slightly larger, thereby limiting a more thorough examination of the linear regime under these experimental conditions. Importantly, noncoherent photon absorption does indeed achieve sensitized upconverted emission, obeying a linear power law in this benchmark composition. The irradiance supplied by the sun (AM 1.5 spectrum) integrated over the entire Q-band absorption profile of PdOEP (475–575 nm) gives 13 mW cm^{-2} (Figure S9) with a corresponding photon flux of $3.5 \times 10^{16} \text{ photons s}^{-1} \text{ cm}^{-2}$ (Figure S10), indicated by the green vertical line in Figure 4. This flux is positioned above the threshold necessary for achieving linear power dependence for sensitized triplet fusion in this composition under the experimental conditions employed in Figure 4. Consequently, AM 1.5 one-sun illumination is clearly poised for achieving the highest possible upconversion quantum yield in concentrated vacuum degassed solutions of these two chromophores.

The quantitative explanation to all of the observations herein lies in evaluating two kinetic limits related to $^3A^*$ decay, bearing in mind that the associated upconverted fluorescence intensity (N_F) is proportionate to the square of the $[^3A^*]$ population (eqs 1 and 2):

$$\frac{d[^3A^*]_t}{dt} = -k_T[^3A^*]_t - k_{TT}[^3A^*]_t^2 \quad (1)$$

$$N_F = \int_0^\infty I_F(t) dt = \int_0^\infty \Phi_F k_{TT} [^3A^*]_t^2 \quad (2)$$

where k_T represents all of the unimolecular and pseudo-first-order decay pathways for $[^3A^*]$, k_{TT} is the bimolecular rate constant for TTA, and Φ_F is the fluorescence quantum yield of the acceptor/annihilator. The analytical solution of eq 1 has a variety of formulations, but the one from Bachilo and Weisman is presented here (eqs 3 and 4).²⁵

$$[^3A^*]_t = [^3A^*]_0 \frac{1 - \beta}{e^{k_T t} - \beta} \quad (3)$$

$$\beta = \frac{k_{TT} [^3A^*]_0}{k_T + k_{TT} [^3A^*]_0} \quad (4)$$

In the weak annihilation limit, $k_T > k_{TT} [^3A^*]_0$, and eq 3 reduces to a single exponential decay, $[^3A^*]_t = [^3A^*]_0 \exp(-k_T t)$, which when substituted into eq 2 and time-integrated yields eq 5.

$$N_F = \frac{\Phi_F k_{TT} [^3A^*]_0^2}{2k_T} \quad (5)$$

Therefore, the total emission intensity is proportional to $[^3A^*]^2$ and should be quadratic with respect to the absorbed optical power. This is precisely what occurs in the low power region in Figure 2 (Figure S5) and Figures 3 and 4, and when the excitation is centered on regions of low sensitizer optical density in Figure 3. Incidentally, this is how we analyzed time-resolved photoluminescence data in our first contribution in this area.²⁶ However, in the strong annihilation limit,²⁵ where $k_{TT} [^3A^*]_0 > k_T$, eq 3 simplifies to

$$[^3A^*]_t = \frac{[^3A^*]_0}{1 + k_{TT} [^3A^*]_0 t} \quad (6)$$

After substitution of eq 6 into eq 2 followed by integration with respect to time, one obtains

$$N_F = \Phi_F [^3A^*]_0 \quad (7)$$

In this strong limit, the total upconversion intensity is linearly proportional to $[^3A^*]$ and directly scales with absorbed optical power as described in the recent treatments by the Monguzzi and Schmidt groups.^{12,14,24} The kinetic analysis above is also completely analogous to conventional delayed fluorescence kinetics as described more than 40 years ago in separate treatments by Birks and Parker.^{27,28} We note that similar rate equations have also been used to rationalize the various power laws governing upconversion in lanthanide materials.²⁹

The laser excitation experiment performed in argon-degassed toluene produced the linear region in Figure 2 when the largest optical powers were provided. Similarly, in vacuum degassed toluene when lamp excitation was utilized, deviations from quadratic behavior scaled with sample absorption (Figure 3) in addition to incident light power, eventually approaching linear

behavior even under these benign excitation conditions. With further increases in the sensitizer concentration, we were able to achieve purely linear behavior using noncoherent photons (Figure 4). However, in these latter experiments, the power threshold, indicating the initial crossover between quadratic to linear, occurred at lower incident power, as k_T was markedly reduced when pseudo-first-order dioxygen quenching was largely eliminated as a competing pathway in $^3A^*$ decay.¹⁴ The strong annihilation regime is where the highest possible upconversion efficiencies can be achieved in a given composition,^{24,27} idyllically occurring at the lowest possible noncoherent (sun)light fluence. Nonetheless, the combination of experimental data and kinetic analysis presented here leaves little doubt that a variety of power dependencies will necessarily result when photochemical upconversion based on sensitized TTA is mechanistically operable, regardless of the nature of the excitation source.

A variety of important conclusions are derived from the present study. One is the realization that the highest attainable photochemical upconversion efficiencies will necessarily be realized in samples that strongly deviate from quadratic incident power behavior. In essence, the first-order processes in eq 1 should be rate limiting with respect to the corresponding second-order annihilation. One means to this end is to ensure that k_T is as small as possible by reducing the energy-wasting pseudo-first-order quenching processes as much as possible, i.e., by using vacuum degassed solvents or oxygen impermeable host media. Of course, the pumping wavelength(s) and the associated sensitizer optical densities, along with the triplet-state photophysics of the acceptor/annihilator are of vital importance to achieve the strong annihilation limit at the lowest possible optical powers. This linear regime was experimentally realized using noncoherent photons at solar power densities, implying that nonconcentrated terrestrial sunlight is able to achieve annihilation-limited upconversion and therefore the highest possible quantum efficiencies. The key finding here is that lasers are simply not required to access the experimental conditions necessary for annihilation-dominated photophysics. In terms of establishing the sensitized TTA mechanism using steady-state illumination, the upconverted photoluminescence response should be evaluated over several decades of incident optical power to demonstrate transitioning between both kinetic limits. At the very least, an incident quadratic dependence should be verified at the lowest fluxes to correctly invoke this mechanism as potentially operative. The lessons provided in this contribution should be quite valuable for optimizing efficiencies in past, present, and future photochemical-based upconversion compositions pumped by solar photons.

■ ASSOCIATED CONTENT

● Supporting Information

Additional data and experimental procedures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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