Annihilation Limit of a Visible-to-UV Photon Upconversion Composition Ascertained from Transient Absorption Kinetics

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Annihilation Limit of a Visible-to-UV Photon Upconversion Composition Ascertained from Transient Absorption Kinetics

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ABSTRACT: Noncoherent sensitized green-to-near-visible upconversion has been achieved utilizing palladium(II) octaethylporphyrin (PdOEP) as the triplet sensitizer and anthracene as the energy acceptor/annihilator in vacuum degassed toluene. Selective 547 nm excitation of PdOEP with incident irradiance as low as 600 μW/cm^2 results in the observation of anthryl fluorescence at higher energy. Stern−Volmer analysis of the dynamic phosphorescence quenching of PdOEP by anthracene possesses an extremely large K_{SV} of 810 000 M^{-1}, yielding a triplet−triplet energy transfer quenching constant of 3.3×10^9 M^{-1} s^{-1}. Clear evidence for the subsequent triplet−triplet annihilation (TTA) of anthracene was afforded by numerous experiments, one of the most compelling was an excitation scan illustrating that the Q-band absorption features of PdOEP are solely responsible for sensitizing the anti-Stokes fluorescence. The upconverted emission intensity with respect to the excitation power was shown to vary between quadratic and linear using either coherent or noncoherent light sources, illustrating the expected kinetic limits for the light producing photochemistry under continuous wave illumination. Time-resolved experiments directly comparing the total integrated anthracene intensity/time fluorescence data produced through upconversion (λ_{ex} = 547 nm, delayed signal) and with direct excitation (λ_{ex} = 355 nm, prompt signal) under conditions where the laser pulse is completely absorbed by the sample reveal annihilation efficiencies of approximately 40%. Similarly, the delayed fluorescence kinetic analysis reported by Schmidt and co-workers (*J. Phys. Chem. Lett.* **2010**, *1*, 1795−1799) was used to reveal the maximum possible efficiency from a model red-to-yellow upconverting composition and this treatment was applied to the anthryl triplet absorption decay transients of anthracene measured for the PdOEP/anthracene composition at 430 nm. From this analysis approximately 50% of the anthryl triplets that decay by TTA produce singlet fluorescence, consistent with the notion that annihilation spin statistics does not impose efficiency limits on upconversion photochemistry.
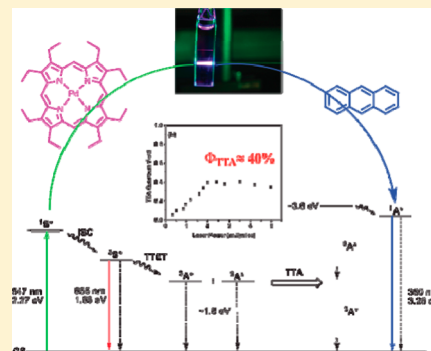
INTRODUCTION

Sensitized triplet−triplet annihilation (TTA) is a regenerative photochemical process resulting in the frequency upconversion of light.[1,2] This technology appears well poised to assist photovoltaics in exceeding the Shockley−Queisser limit by enabling the capture and conversion of sub-bandgap light, thereby creating an improved spectral match to the solar spectrum.[3] Along these lines, noncoherent upconversion has recently been exploited for the capture and conversion of sub-bandgap photons in a WO$_3$ photoelectrochemical cell,[4] has been shown to operate on ZrO$_2$ nanostructured insulator surfaces,[5] has been used to low energy sensitize amorphous silicon photovoltaics,[6−8] and has been most recently exploited in solar-driven detoxification.[9] In general terms, photon upconversion is facilitated by selective excitation of strongly absorbing 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 ultimately producing the desired annihilation-producing fluorescence. This research area has clearly undergone an explosion of activity over the past several years.[10−40] 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, and the upconverted photons are easily visualized by the naked eye in many cases. These sequential bimolecular reactions have also been translated into both soft and hard polymer host matrices,[14,18,29,30,37,41] a critical prerequisite for real-world device integration. Importantly, the quantum efficiency of sensitized TTA-based upconversion is not limited by spin statistics and has been shown to have an upper limit exceeding 60% from kinetic analysis of the delayed fluorescence intensity decays in a red-to-yellow upconverting composition.[34] Under continuous wave irradiation, measured quantum efficiencies up to 34% have been recorded to date in solution,[4] also well in excess of the so-called 11.1% spin statistical limit. Similarly, reasonably efficient solid-state photochemical upconversion compositions have also begun to emerge, and a record of 22% quantum efficiency has been recently achieved for green-to-blue conversion in a rubbery urethane host under continuous wave laser excitation.[37]

Scheme 1. Qualitative Jablonski Diagram Illustrating Sensitized TTA-Based Upconversion Occurring between PdOEP and Anthracene[a]
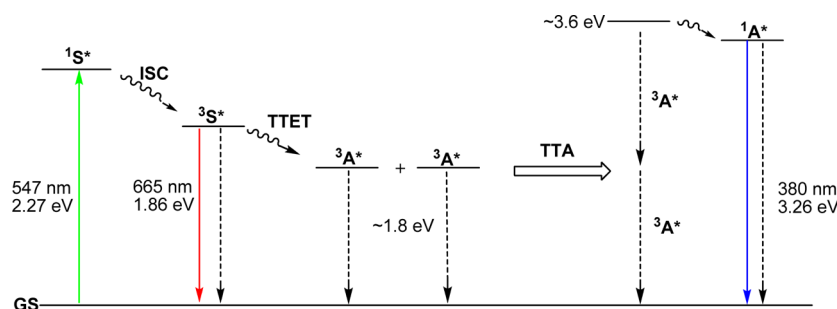
[a]GS = ground state, S = sensitizer = PdOEP, ISC = intersystem crossing, TTET = triplet−triplet energy transfer, TTA = triplet−triplet annihilation, A = acceptor = anthracene.

The present contribution evaluates the performance of the PdOEP/anthracene composition in vacuum degassed toluene under a variety of experimental conditions, producing an impressive green-to-near visible upconversion potentially useful for the capture and conversion of sub-bandgap photons to drive the excitation of wide-bandgap semiconductors such as TiO_2. Scheme 1 presents the associated Jablonski diagram illustrating the energetics of these two chromophores. We note that the related PtOEP/anthracene combination on dendrimer supports in aqueous solution was reported to demonstrate an environment-responsive upconversion.[42] The combined light absorption and triplet quenching metrics of the PdOEP/anthracene mixture made it possible to observe an upconversion detected excitation spectrum in sensitized TTA photochemistry for the first time. Incident continuous wave light power dependence studies revealed that this composition exhibited anti-Stokes fluorescence whose intensity with respect to the excitation power varied between quadratic and linear using both coherent and noncoherent light sources, thereby illustrating the weak and strong annihilation kinetic regimes, respectively.[31,33,38] In order to evaluate the maximal upconversion yield that can be achieved in the present composition, we directly measured the TTA efficiency as a function of incident laser pulse energy and adapted the delayed fluorescence intensity decay analysis developed by Schmidt and co-workers[34] to the transient absorption decay kinetics of sensitized triplet anthracene.

■ EXPERIMENTAL SECTION

General Information. Palladium(II) octaethylporphyrin (PdOEP) was purchased from Frontier Scientific. Gold label anthracene was purchased from Aldrich and used without further purification. Spectroscopic grade toluene was purchased from Aldrich and used as received.

Photophysical Measurements. Static absorption spectra were measured with a Cary 50 Bio UV−vis spectrophotometer from Varian. Steady-state photoluminescence spectra were recorded using a QM-4/2006SE fluorescence spectrometer from Photon Technologies Incorporated or a FL/FS920 spectrometer from Edinburgh Instruments. Excitation was achieved by the 514.5 nm line from an Ar^+ laser (Coherent Innova 70C) isolated with a bandpass filter or a 450 W Xe arc lamp equipped with a monochromator and appropriate long pass filters. The incident laser or lamp power was varied using a series of neutral density filters placed directly in front of the sample. All luminescence samples were prepared in a specially designed 1 cm^2 optical cell bearing a side arm roundbottomed

flask and were subjected to a minimum of three freeze−pump−thaw degas cycles prior to all measurements. The laser and lamp power were measured using either a Molectron Power Max 5200 power meter or an Ophir Nova II/PD300-UV power meter, respectively. The phosphorescence intensity decays of anthracene quenched PdOEP were measured using a nitrogen-pumped broadband dye laser (2−3 nm fwhm) from PTI (model GL-3300 N_2 laser and model GL-301 dye laser) used to selectively excite the low energy PdOEP Q-band with an apparatus that has previously been described.[43] The PdOEP luminescence intensity decays were fit using Origin 8.1 and were all adequately modeled using a single exponential function.

Nanosecond transient absorption measurements were collected on a LP 920 spectrometer from Edinburgh Instruments where ΔA remained linear up to 0.8 O.D. in single wavelength acquisition mode detecting at 430 nm; here the ground state absorption of the samples utilized was 0.126 at 430 nm. Excitation of the samples in these experiments was accomplished using a Nd:YAG/OPO laser system from Opotek (Vibrant LD 355 II) operating at 1 Hz. The incident laser power was varied using a series of neutral density filters or by appropriately modifying the Q-switch delay. Single wavelength absorption transients were kinetically analyzed using Origin 8.1. The same spectrometer was also equipped with an Andor iStar iCCD detector that permitted the collection of time-resolved emission spectra used in the determination of TTA quantum efficiencies (Φ_{TTA}) from prompt and delayed fluorescence signals as described previously.[33] In the present donor−acceptor/annihilator mixture, the delayed fluorescence spectrum was integrated for 1 ms immediately after the 547 nm laser pulse, capturing the delayed fluorescence signal in its entirety. The prompt fluorescence spectrum, due to the direct excitation of the anthracene at 355 nm, was integrated from just before the laser pulse until after all of the fluorescence decayed completely. Here, the yield of delayed fluorescence (F_d) from anthracene was measured after selective excitation of the PdOEP sensitizer ($\lambda_{ex} = \lambda_d = 547$ nm), which was directly compared to that of the prompt fluorescence (F_p) from anthracene measured in the identical composite sample, observed by exciting this acceptor directly at 355 nm (λ_p). A mixture of 43 μM PdOEP and 0.35 mM anthracene in freeze−pump−thaw degassed toluene was used for detecting the prompt and delayed fluorescence signals. The mixture had identical optical density (O.D. = 2.0) at their respective excitation wavelengths of 355 and 547 nm; therefore. 100% of the excitation photons are absorbed and generate excited

singlets to approximately the same depth in each experiment. In both instances, the anthryl fluorescence is produced in identical environments and the TTA yield is readily calculated as a function of pulse energy using eq 1.

$$\Phi_{\text{TTA}} = \frac{2F_d E_p \lambda_d}{F_p E_d \lambda_p} \qquad (1)$$

Here E_d and E_p are the respective laser pulse energies and the factor of 2 in the numerator scales the annihilation yield to unity, as two excited triplets are necessary to produce one triplet fusion product. This expression assumes that the fluorescence quantum yield of anthracene is the same regardless of whether it is produced through direct excitation or sensitized through TTA.
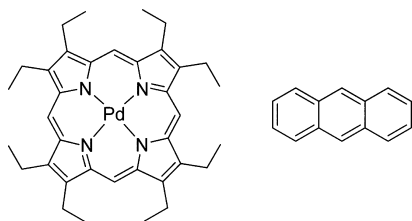
■ RESULTS AND DISCUSSION

The chemical structures of both the PdOEP sensitizer and anthracene acceptor investigated in this study are presented
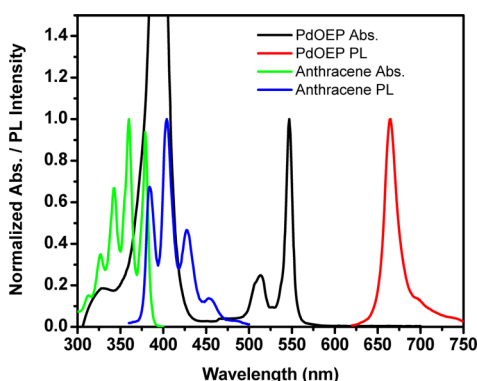

Figure 1. Normalized absorption and emission spectra of PdOEP and anthracene measured in toluene.

below along with their normalized ground state absorption and emission spectra measured in toluene, Figure 1.

The PdOEP sensitizer, whose phosphorescence is 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 (λ_{max} = 513 nm, 547 nm). Anthracene's $\pi-\pi^*$ absorption bands all lie below 400 nm ensuring that porphyrin Q-band excitation will result in selective excitation of only the triplet sensitizer. In order to examine the quenching of the triplet excited state of PdOEP by anthracene, the luminescence intensity decay of the former was evaluated as a function of anthracene concentration in vacuum degassed toluene solutions; each decay curve was adequately fit to a single exponential function from which excited state lifetimes were easily extracted. The dynamic Stern−Volmer plot generated from these lifetime measurements revealed a very large Stern−Volmer constant (K_{SV}) of 810 000 M^{-1}, Figure 2.
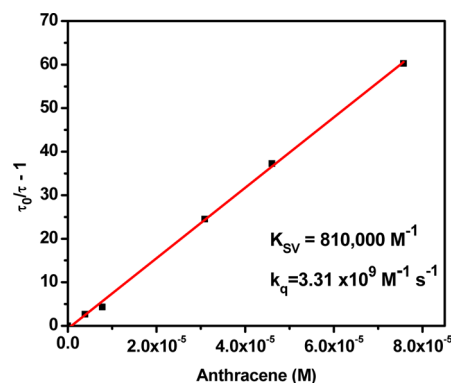

Figure 2. Stern−Volmer analysis of dynamic quenching between PdOEP and anthracene in vacuum degassed toluene.

In absence of a quencher, the triplet excited state lifetime of PdOEP in vacuum degassed toluene (several freeze−pump−thaw cycles) was measured to be 245 μs under these experimental conditions, yielding a bimolecular energy transfer quenching rate constant (k_q) of 3.3×10^9 M^{-1} s^{-1}. The large observed K_{SV} value is consistent with the long lifetime of the sensitizer being utilized and the exothermicity of the energy transfer process between energized PdOEP and anthracene. The PdOEP phosphorescence quenching was verified to proceed through triplet−triplet energy transfer as ascertained by independent laser flash photolysis experiments showing that the T$_1$ → T$_n$ absorption spectrum of ^{3}An* was exclusively produced following selective excitation of PdOEP, Figure 3c. Figure 3, panels a and b, depicts the transient absorption difference spectra of PdOEP (λ_{ex} = 547 nm) and anthracene (λ_{ex} = 355 nm) measured as a function of delay time and illustrate the characteristic differences between the T$_1$ → T$_n$ absorptions in each chromophore. The complete lack of a bleaching signal at long delay times in the PdOEP/anthracene composition (Figure 3c) concomitant with identical transient features as seen in Figure 3b clearly demonstrates complete transfer of absorbed photons to sensitized anthryl triplets in the chromophore mixture. In all experiments performed, no evidence for anthracene dimerization was obtained,[15] likely as a result of using modest anthracene concentrations.

Figure 4 presents the double logarithmic plot generated from the intensity of the singlet fluorescence emanating from anthracene at 430 nm measured as a function of incident power density over several decades when PdOEP is selectively excited using bandpass filtered 514.5 nm output from an Ar$^+$ laser. The double logarithmic plot provides a good illustration of the changeover in the power law responses occurring as a result of changes in kinetic regime dominating triplet state decay in the acceptor/annihilator as described below. We chose 430 nm as the monitoring wavelength as it was largely free of the inner-filter artifacts that suppressed the anthryl fluorescence at shorter wavelengths. As anticipated, at low incident power, the slope of this plot is 2.0 indicative of quadratic dependence. 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, illustrating the anticipated kinetic limits for the photochemical upconversion process as shown previously by Monguzzi et al.,[31] the Schmidt group,[33] and this laboratory.[37,38]
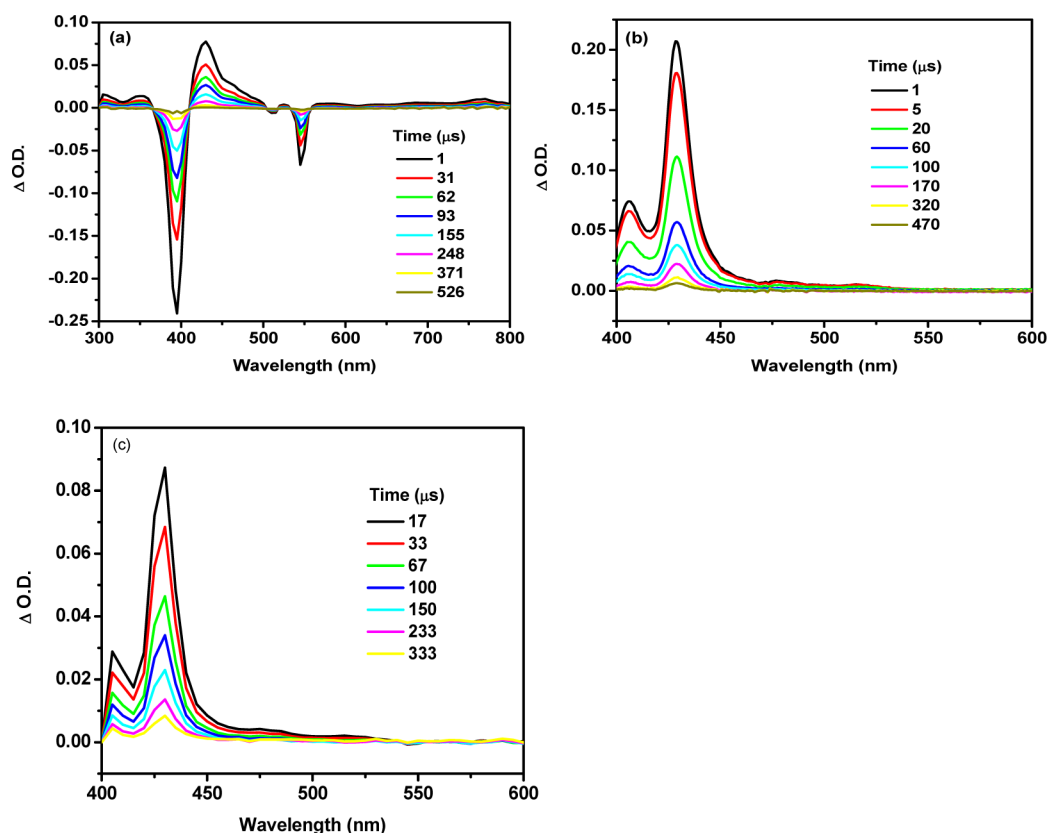
Figure 3. (a) Transient absorption difference spectrum of 8 μM PdOEP in freeze−pump−thaw degassed toluene measured at several delay times, 3.0 mJ/pulse, λ_{ex} = 547 nm. (b) Transient absorption difference spectrum of 0.14 mM anthracene in freeze−pump−thaw degassed toluene measured at several delay times, 3.0 mJ/pulse, λ_{ex} = 355 nm. (c) Transient absorption difference spectrum of 8 μM PdOEP and 0.29 mM anthracene in freeze−pump−thaw degassed toluene measured at several delay times following selective excitation of PdOEP, 3.0 mJ/pulse, λ_{ex} = 547 nm.
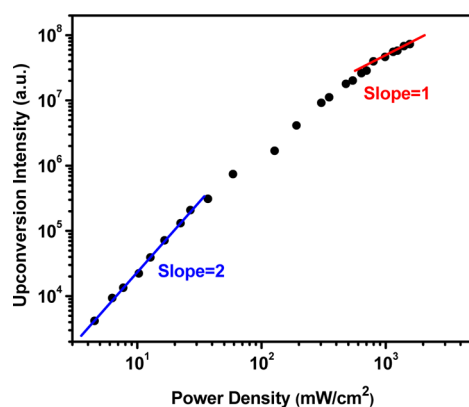
Figure 4. Double logarithmic plot of the upconversion emission signal at 430 nm measured as a function of 514.5 nm incident laser power density in a mixture of PdOEP (9 μM, O.D. @ 515 nm = 0.15) and anthracene (0.12 mM) in freeze−pump−thaw degassed toluene. The solid lines are the linear fits with slopes of 1.0 (red, linear response) and 2.0 (blue, quadratic response) in the high and low power regimes, respectively.

Since it is desirable to evaluate upconversion compositions intended for solar photon capture and conversion, noncoherent excitation was also applied to the identical samples as described above in Figure 5. In all instances, the power densities were recorded immediately in front of the sample and a conventional single photon counting fluorimeter was used to collect all of the subsequent data. Figure 5 presents the normalized upconversion intensities at 430 nm recorded in a mixture of 37 μM

PdOEP and 0.4 mM anthracene plotted as a function of the normalized noncoherent incident power density measured at two distinct wavelengths in the Q-band region of the PdOEP sensitizer, λ_{ex} = 530 and 547 nm. Similar to the laser excitation experiments, quadratic and linear power dependence was achieved in this sample, albeit using different portions of the Q-band region where the sample optical densities were extremely different. At 530 nm, where the Q-band region has minimal absorption, a quadratic dependence was produced consistent with low numbers of absorbed photons in the weak annihilation limit, Figure 5a. However, 547 nm noncoherent excitation pumps the strongest Q-band absorption feature and produces linear upconversion response with respect to absorbed optical power, illustrative of strong annihilation limit behavior. As we have discussed previously,[38] achieving this desirable saturation limit is simply a matter of generating large numbers of sensitized triplets and this is enabled either by large incident photon flux (concentrated light beams) or by absorbing large numbers of photons by the sensitizer; the latter is simply controlled by concentration. Additionally, to ensure that the sensitized triplets react bimolecularly via TTA and not through pseudofirst-order quenching with dissolved dioxygen, vacuum degassed solutions substantially minimize the latter.

Since the experiments above were recorded in a conventional fluorimeter, we decided to take advantage of all of its functionality in the present case. Additional clear-cut evidence supporting the PdOEP-sensitized triplet−triplet annihilation of anthracene was afforded by an "anti-Stokes" excitation scan, which illustrated that the Q-band absorption features of PdOEP

Figure 5. Normalized upconversion intensity in a mixture of 37 μM PdOEP and 0.4 mM anthracene at 430 nm plotted as a function of (a) normalized 530 nm and (b) normalized 547 nm incident power density output from the long-pass filtered Xe lamp/monochromator light source. The solid blue lines are intended to illustrate quadratic power dependence and the solid red lines demonstrate linear power dependence.

are indeed responsible for sensitizing anthracene fluorescence at higher energy. To the best of our knowledge this is the first experiment of this kind to be reported in sensitized TTA and can likely be immediately extended to other low power upconverting compositions. We purposely chose experimental conditions (high PdOEP concentrations) that would produce linear power dependence throughout the Q-band region of the spectrum. We note that if linear dependence could not be achieved in the present composition, then the excitation profile would need to be compared to the square of the associated absorption spectrum as has been recently shown in a molecular-sensitized upconverting lanthanide nanomaterial.[44] Additionally, front face detection was employed to avoid the Soret band-based inner filter artifacts associated with using large PdOEP concentrations in these experiments. The upconversion excitation profile was measured at lower energy (480−570 nm) with respect to the position of emission monitoring (430 nm) and the resultant normalized data is presented in Figure 6 (red line), which is directly compared to the normalized absorption profile of the PdOEP Q-bands (black line). Without question, the PdOEP Q-bands are indeed responsible for the sensitization of anthryl fluorescence observed in the near visible portion of the spectrum that must be occurring through sensitized triplet fusion.

Figure 6. Upconversion excitation spectrum generated in a mixture of PdOEP/anthracene in vacuum degassed toluene while monitoring emission at 430 nm (red line), which is compared to the ground state absorption spectrum of PdOEP (black line).

Figure 7a presents the combined time-resolved fluorescence spectra resulting from sensitized TTA photochemistry (delayed fluorescence spectra, λ_{ex} = 547 nm, solid lines) and from direct excitation (prompt fluorescence spectrum, λ_{ex} = 355 nm, 1 mJ/pulse, dashed black line) of a sample of 43 μM PdOEP and 0.35 mM anthracene contained in vacuum degassed toluene at RT. All anthryl fluorescence below 400 nm is completely attenuated as a result of reabsorption as discussed earlier, primarily by the Soret band of the porphyrin. As the molecular fluorescence emanates from the identical environment, this trivial fluorescence quenching cancels (the same effect is imparted in both delayed and prompt experiments) and eq 1 can be used to calculate the TTA yield as a function of laser pulse energy from these data.[33] Direct application of eq 1 to the data in Figure 7a produced the calculated values of Φ_{TTA} as shown in Figure 7b. As shown previously, the TTA yield increases with increasing laser pulse energy until a plateau is reached, in this particular instance near 2 mJ/pulse indicating that the process has saturated, identical to that when linear incident power dependence is achieved in related cw experiments, Figures 4 and 5. As stated by Schmidt and co-workers, the numerator and denominator in eq 1 both scale linearly once this plateau is reached, indicating that the efficiency for the process has reached its maximal limit.[33]

Under saturation conditions, the TTA efficiency approaches 40% in this composition, well above the so-called annihilation spin statistical limit of 11.1%, providing yet another example of a relatively efficient TTA process largely exceeding an incorrect presumptuous theoretical limit.[33] If one uses this data in concert with the measured absolute quantum yield of anthracene measured under identical experimental conditions (0.25), an upconversion quantum efficiency (Φ_{UC} = $\Phi_{ISC}\Phi_{q}\Phi_{TTA}\Phi_{f}$)[22,33] of 0.10 is calculated (here Φ_{q} = 0.99), and this is notably limited in magnitude by its singlet fluorescence quantum yield and not by Φ_{TTA}. In order to properly evaluate maximum TTA efficiencies, triplet sensitization experiments performed under optically saturated conditions are necessary, otherwise significantly conservative numbers are obtained.[45] Such latter values can be completely correct for the experimental conditions utilized but do not adequately reflect the maximal TTA yields that can be realized for a given acceptor/annihilator. The calculated Φ_{TTA} values derived from the current experiments are important, as they will be used in concert with various kinetic parameters extracted from transient absorption triplet decay data to characterize the

Figure 7. (a) iCCD detected delayed fluorescence spectra in 43 μM PdOEP and 0.35 mM anthracene contained in vacuum degassed toluene obtained with various laser pulse energies at 547 nm (solid lines). The black dashed line is the prompt fluorescence spectrum of anthracene measured in the same sample obtained with a 1.0 mJ laser pulse at 355 nm. These data are illustrative of the significant inner filtering at high energies inherent in these samples but importantly do not affect the calculated TTA yields. (b) Calculated TTA quantum yields as a function of incident laser pulse energy using the data from (a) and eq 1.

Table 1. Parameters Obtained from the Fits to the Sensitized Anthryl Transient Absorption Decays at 430 nm to eq 4[a]

pulse energy (mJ)	$[^3M^*]_0$ (10^{-5} M)	k_T (10^3 s^{-1})	β	α (10^4 s^{-1})	k_{TT} (10^9 M^{-1} s^{-1})	f_{TT}	Φ_{TTA}	η_{conv}	ϕ_0
1.8	1.1	7.0	0.894	5.9	5.3	0.734	0.34	0.46	0.41
2	1.2	6.5	0.908	6.4	5.5	0.758	0.40	0.52	0.48
2.4	1.4	7.2	0.910	7.3	5.2	0.761	0.40	0.53	0.48
2.8	1.6	6.9	0.923	8.3	5.2	0.786	0.38	0.49	0.45
3.5	1.9	7.2	0.929	9.4	4.9	0.798	0.41	0.51	0.47

[a]See text for descriptions of the kinetic fit parameters.

efficiency limit (at the highest sensitized acceptor/annihilator concentration) for annihilation in the PdOEP/anthracene composition.

The sensitized acceptor/annihilator population decays through parallel first and second-order pathways according to the rate equation:

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

where k_T is the first-order triplet decay rate constant, k_{TT} is the triplet–triplet annihilation rate constant, and the excited triplet concentration varies with time as $[^3M^*]_t$. The analytical solution to eq 2 is well established as[34,38,46]

$$\frac{[^3M^*]_t}{[^3M^*]_0} = \frac{1 - \beta}{\exp(k_T t) - \beta} \qquad (3)$$

with $\beta = \alpha/(k_T + \alpha)$ and $\alpha = k_{TT}[^3M^*]_0$, where $[^3M^*]_0$ is the initial sensitized triplet concentration and β equates to the initial fraction of triplet decay occurring through the bimolecular TTA channel. Equation 3 can be written in terms of transient absorption parameters where the triplet concentrations are directly proportional to the their corresponding ΔA values

$$\Delta A_t = \frac{\Delta A_0 (1 - \beta)}{\exp(k_T t) - \beta} \qquad (4)$$

Nonlinear least-squares fitting of eq 4 to the measured transient absorption decays for triplet anthracene at 430 nm recorded as a function of laser pulse energy yielded the three unknown parameters ΔA_0, β, and k_T; ΔA_0 is readily converted into $[^3M^*]_0$ using the established extinction coefficient for triplet anthracene at 430 nm, 42 000 M^{-1} cm^{-1},[16] whereas β and k_T

permit the calculation of α and therefore k_{TT}. Table 1 collects all relevant parameters derived from this kinetic analysis. A representative example of the transient absorption decay fitting using eq 4 is given in Figure 8, where the red line represents the
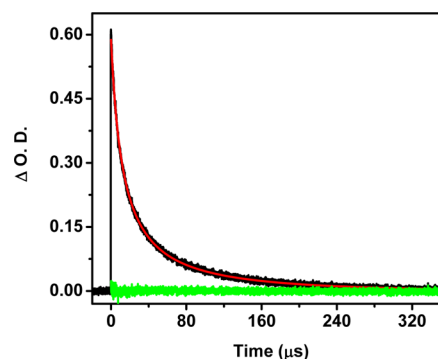
Figure 8. Representative transient absorption kinetic decay (black) of triplet anthracene at 430 nm produced using 547 nm excitation (2.4 mJ/pulse) in a mixture of 43 μM PdOEP and 0.35 mM anthracene in freeze–pump–thaw degassed toluene. The red line is the kinetic fit to eq 4 and the green line is the residuals of the fit.

fit to the data in black and the residuals to the fit is provided in green. Similar random distribution of the residuals was observed for all of the laser pulse energies investigated, indicative of the adequacy of the fits to the eq 4 kinetic model. It is important to note that the rate constants for both first- (k_T) and second-order (k_{TT}) anthracene triplet state decay measured in the present experiments are quantitatively similar to those measured by Saltiel and co-workers in 1981.[47] We also fit the delayed fluorescence decay curves using exactly the approach published by Schmidt and co-workers[34] applied to the

present case, however, these fits were not nearly as satisfactory with respect to that obtained using the transient absorption data. Similar to the delayed fluorescence kinetic analysis, the fraction (f) of triplets decaying by first- and second-order processes can be normalized as $f_T + f_{TT} = 1$, and we are most concerned with f_{TT}, calculated from the fits to eq 4 using eq 5.

$$f_{TT} = 1 - \frac{\beta - 1}{\beta} \ln(1 - \beta) \tag{5}$$

The efficiency of bimolecular quenching of sensitized triplets to yield fluorescent anthryl singlet acceptor states is $\eta_{conv} = \Phi_{TTA}/f_{TT}$ and the initial annihilation efficiency, $\phi_0 = \beta\eta_{conv}$, is demonstrative of the best case scenario where the concentration of sensitized anthryl triplets is at its highest. In the present experiments, η_{conv} and ϕ_0 slightly exceed 40% at all pulse energies evaluated (Table 1), consistent with the notion that anthracene triplets undergo TTA in such a manner that all of the quintet states and at least 1/2 of the triplet states in the annihilation reaction are returned to the bath as excited anthryl triplets.[34]

CONCLUSIONS

The current experiment demonstrated that selective excitation of PdOEP at 547 nm with low power noncoherent photons in the presence of anthracene in vacuum degassed toluene results in upconverted near-visible anthracene fluorescence. The upconverted emission intensity with respect to the excitation power can vary between quadratic and linear using either coherent or noncoherent light sources. For the first time, an upconversion excitation scan was successfully recorded for a sensitized TTA donor/acceptor pair. Evaluation of the prompt and delayed fluorescence signals from this composition showed that the anthryl TTA quantum efficiency approaches 40%, exceeding that of its singlet fluorescence yield (25%), implying that the latter will necessarily limit upconversion-generated fluorescence in this instance, $\Phi_{UC} = 0.10$. Transient absorption kinetic analysis of the anthryl triplet decay illustrated that approximately 50% of the anthryl triplets that decay by TTA produce singlet fluorescence, consistent with the notion that annihilation spin statistics does not impose efficiency limits on upconversion photochemistry.

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Notes
The authors declare no competing financial interest.

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