

**PCCP****Photochemical upconversion is suppressed by high concentrations of molecular sensitizers**

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Complete List of Authors:	Gholizadeh, Elham; The University of New South Wales, School of Chemistry Frazer, Laszlo; Monash University, School of Chemistry; The University of New South Wales, School of Chemistry MacQueen, Rowan; Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Institute for Nanospectroscopy Gallaher, Joseph; The University of New South Wales, School of Chemistry Schmidt, Timothy; The University of New South Wales, School of Chemistry

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Photochemical upconversion is suppressed by high concentrations of molecular sensitizers †

 Elham Morteza Gholizadeh,^{*a} Laszlo Frazer,^{a,b} Rowan W. MacQueen,^{a,c} Joseph K. Gallaher,^a and Timothy W. Schmidt^a

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Photochemical upconversion uses sensitized triplet-triplet annihilation in bimolecular compositions to convert lower energy photons to higher energy photons. For high efficiency under low illumination, usually a high sensitizer concentration is desirable. However, here we show that the upconversion sensitizer can reduce the emitter triplet lifetime by dynamic quenching, with rate constants on the order $10^6 \text{ M}^{-1} \text{ s}^{-1}$, leading to diminishing returns beyond a certain concentration. These results serve as a warning to designers of photochemical upconvertors that higher concentrations of sensitizers are not necessarily beneficial to upconversion performance.

1 Introduction

A solar cell with a single absorption threshold is limited to an energy conversion efficiency of 33.7% under the AM1.5G solar spectrum (the Shockley-Queisser limit).^{1–3} Especially for higher band gap solar cells such as the emerging perovskite family^{4,5}, a large part of the efficiency loss is a result of the inability to harvest photon energies below the band gap.⁶ Photon upconversion is a process which converts one or more below-band gap photons to energies above the band gap, such that they can be used by a solar cell.⁷ A cell which efficiently harnesses photon upconversion increases the maximum efficiency by 9.7 percentage points to 43.4%.^{7,8}

Photochemical upconversion is such a process.^{9–12} It has been implemented in several types of devices with low cost, low toxicity designs.^{13–23} While there are many instances of high efficiencies being attained under monochromatic radiation,^{24,25} for solar energy purposes, a high efficiency must be achieved under the broadband, relatively weak solar spectrum.

In photochemical upconversion, which is an incoherent form of photon upconversion applicable to the solar spectrum, the energy of sequentially absorbed photons is stored as triplet states. The efficiency of photochemical upconversion rests on the competi-

tion between the annihilation of triplets and their decay by other means.²⁶ As such, it is desired to operate under conditions with a high triplet concentration so that annihilation predominates. In order to reach such conditions, the concentration of absorbed photons per unit time must be high, which is determined by the concentration of sensitizer molecules, their extinction coefficient, and the photon flux. From this perspective, a high concentration of sensitizers will be desired.^{8,27}

In this manuscript, we show that as sensitizer concentrations increase, they quench emitter triplet states, disrupting energy storage and ultimately leading to a reduced upconversion efficiency. We model the behaviour kinetically and measure quenching rate constants using a Stern-Volmer analysis of delayed fluorescence kinetics.

2 Naïve Kinetic Model

Figure 1 outlines the five steps that lead to the conversion of low energy light to fluorescence at a higher energy. Two species are required: a sensitizer^{28–33} and an emitter.^{34,35} Briefly, sensitizer molecules absorb lower energy photons and undergo efficient and fast intersystem crossing. The sensitizer triplets are efficiently and rapidly quenched by ground state emitter molecules, resulting in a population of triplet emitter molecules by triplet energy transfer (TET).

The concentration of triplets in the emitter molecules evolves according to the well-known rate equation^{36–39}

$$\frac{d[{}^3E]}{dt} = k_{\phi}(z)[S] - k_1[{}^3E] - k_2[{}^3E]^2, \quad (1)$$

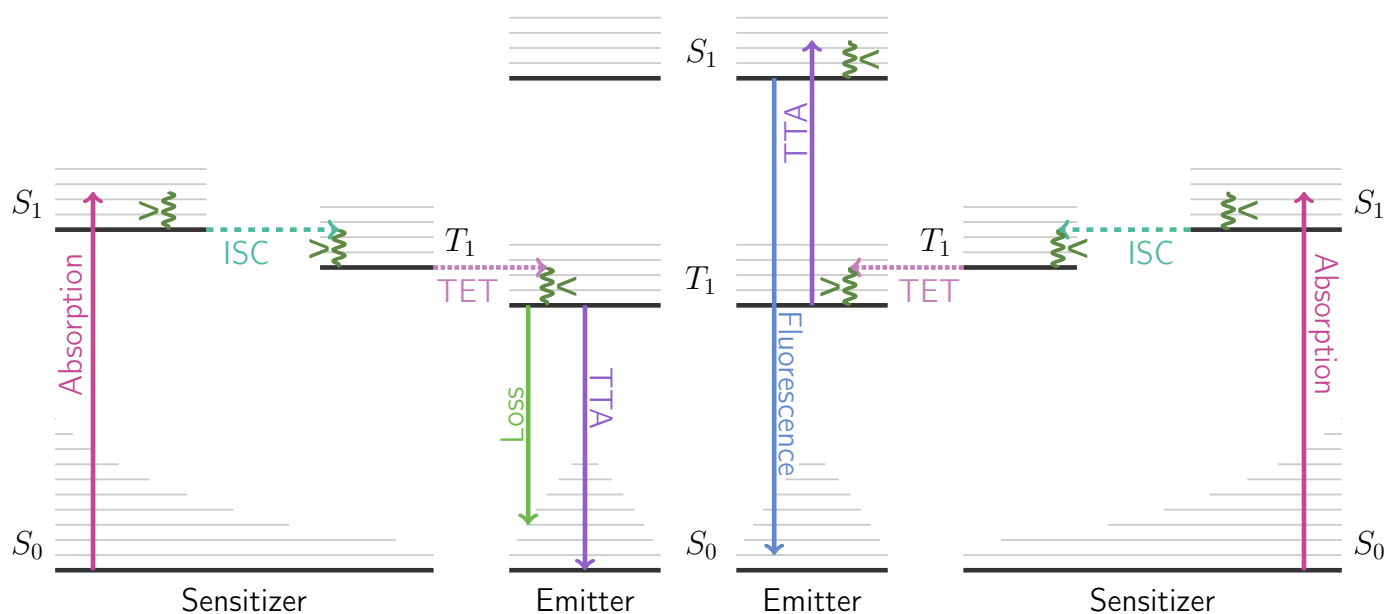
where $[{}^3E]$ is the emitter triplet concentration, $k_{\phi}(z)$ is the excitation rate per sensitizer, which depends on the depth z in the device, $[S]$ is the sensitizer concentration, k_1 is the triplet decay

^a ARC Centre of Excellence in Exciton Science, School of Chemistry, UNSW, Sydney, NSW 2052, Australia.

^b ARC Centre of Excellence in Exciton Science, School of Chemistry, Monash University, Box 23, VIC 3800, Australia.

^c Helmholtz-Zentrum Berlin für Materialien und Energie, 12489 Berlin, Germany.

† Electronic Supplementary Information (ESI) available: Photochemical upconversion action spectra, upconversion yields as a function of irradiance, additional triplet decay rate measurements as a function of sensitizer concentration, additional Stern-Volmer measurements of rate constants, steady state absorption and emission spectra. See DOI: 10.1039/b000000x/



Photochemical Upconversion Processes

1. Sunlight Absorption
2. Intersystem Crossing
3. Triplet Energy Transfer
4. Triplet-Triplet Annihilation
5. Fluorescence

Vibrational Relaxation Provides Ratchet

Triplet Loss Owing to Nonradiative and Radiative (Spin-Orbit) Mechanisms

Fig. 1 Diagram of the five steps of the photochemical upconversion process.

rate of the emitter, and k_2 is the triplet-triplet annihilation rate constant.

Where upconversion is relatively inefficient, under steady-state conditions Equation 1 reduces to

$$[{}^3E] = \frac{k_\phi(z)[S]}{k_1}. \quad (2)$$

The rate of excitation diminishes as the photon stream propagates into the device. Under a single excitation wavelength, λ , this dependence is

$$k_\phi(z) = k_\phi(0) \exp(-\varepsilon'(\lambda)[S]z) \quad (3)$$

Integrating over z , the rate of photochemical upconversion, W_{UC} , in a device much thicker than the absorption length is

$$W_{UC} = \eta_c \Phi_F k_2 [{}^3E]^2 = k_2 \eta_c \Phi_F \frac{k_\phi(0)^2 [S]^2}{4\varepsilon'(\lambda) k_1^2}, \quad (4)$$

where η_c is the proportion of triplet annihilation events which result in excited singlets, Φ_F is the fluorescence quantum yield of the emitter, and $\varepsilon'(\lambda)$ is the natural molar extinction coefficient

at wavelength λ ($\varepsilon' = \log(10)\varepsilon$).

3 Evidence for Quenching

Under the assumption that all the other parameters do not change, upconversion device performance, W_{UC} , should improve linearly as the sensitizer concentration $[S]$ increases. To test this, we used our previously reported action spectrometer⁴⁰ to measure Φ_{TTA} ,²⁴ the proportion of triplets which undergo annihilation, for three different metallo-octaethylporphyrins sensitizing diphenylanthracene (Zn, Pd and Pt). Absorption and emission spectra are shown in Fig. 2 and the ESI[†]. The irradiance-dependence of Φ_{TTA} and example action spectra are available in the ESI[†].

Figure 3 shows the Φ_{TTA} interpolated to one sun irradiance at various concentrations. We found that for all three sensitizers, Φ_{TTA} has a maximum near 0.6 mM. Therefore, these materials will under-perform Eq. 4 at high sensitizer concentrations. Because the emitter-to-sensitizer concentration ratio was held constant at $[E]/[S] = 15$, increasing $[S]$ cannot change the equilibrium statistical distribution of triplets between the sensitizer and the emitter. A small amount of aggregation was detected, as evi-

denced by the appearance of peaks to the red of the Q-band (Figure S1). These peaks have absorbances of 0.05 or less, where the Q-band would absorb at >30 at the same concentration. As such, we do not believe that aggregation is the major effect and hypothesized that the effect is to increase k_1 , thus reducing W_{UC} .

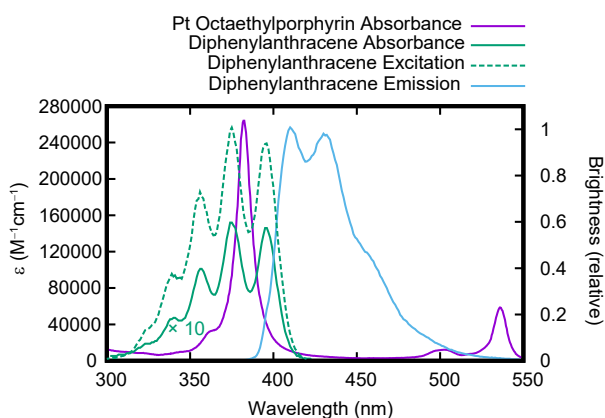


Fig. 2 Absorption spectra of Pt octaethylporphyrin and diphenylanthracene ($\times 10$). Emission and excitation spectrum of diphenylanthracene. Photochemical upconversion occurs when the porphyrin sensitizer is excited in the Q band near 500–550 nm, causing the diphenylanthracene to emit at a shorter wavelength.

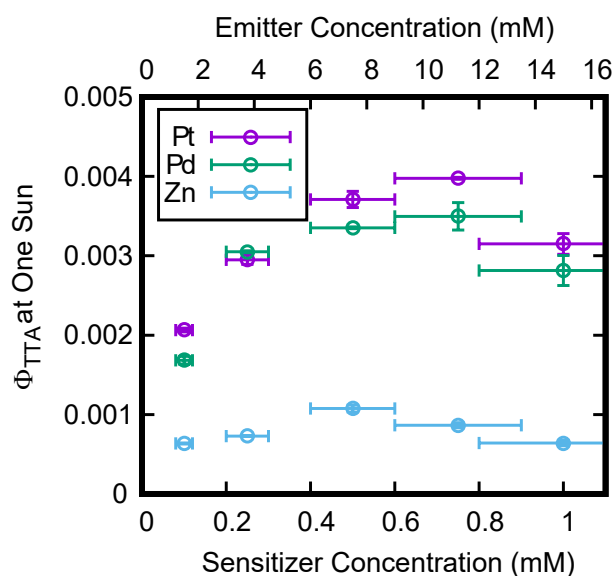


Fig. 3 Yield Φ_{TTA} of photochemical upconversion as a function of concentration. The sensitizers are {Pt, Pd, Zn} octaethylporphyrin and the emitter is diphenylanthracene. The concentration of the sensitizer and emitter were proportional. These action spectroscopy measurements are interpolated to one sun equivalent irradiance.

4 Quenching Model

To accommodate the change in the triplet decay rate as a function of sensitizer concentration, we introduce a new rate constant, k_q . The evolution of the triplet concentration then becomes⁴¹

$$\frac{d[{}^3E]}{dt} = k_\phi(z)[S] - (k_1^0 + k_q[S])[{}^3E] - k_2[{}^3E]^2. \quad (5)$$

k_q has a significant impact on the upconversion rate:

$$W_{UC} \propto \frac{[S]}{(k_1^0 + k_q[S])^2}. \quad (6)$$

This function exhibits a maximum where $k_1^0/k_q = [S]$, and thus for typical emitter decay rates of $k_1^0 \simeq 10^3 \text{ s}^{-1}$, a dynamic quenching rate constant on the order $k_q \simeq 10^6 \text{ M}^{-1} \text{ s}^{-1}$, just 1/10000 the diffusion limit,²⁶ would predict a peak TTA yield at $[S] \simeq 10^{-3} \text{ M}$, as observed in Fig. 3.

As such, the quenching model appears to be a plausible explanation for the results obtained above. To test the hypothesis, we performed kinetic experiments to determine the dependence of the first order decay of triplets on the sensitizer concentration.

5 The Triplet Decay Rate

To measure the triplet dynamics, we recorded the upconversion delayed fluorescence I as a function of time after laser excitation of the sensitizer. Example results for Pt octaethylporphyrin and diphenylanthracene are shown in Fig. 4. Measurements for other sensitizers and emitters are shown in the ESI[†].

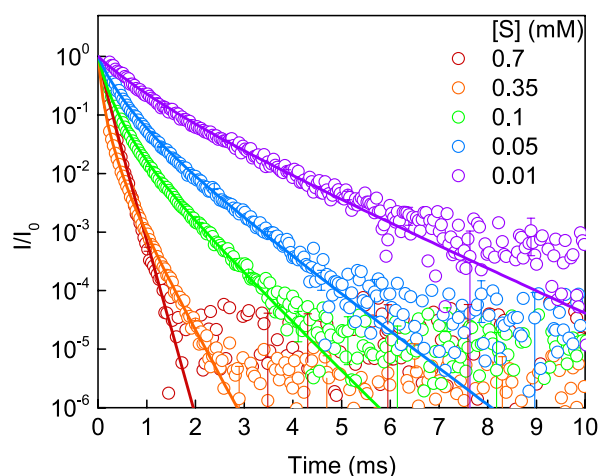


Fig. 4 Brightness of photochemical upconversion as a function of time at various sensitizer concentrations $[S]$. The sensitizer is Pt octaethylporphyrin and the emitter is diphenylanthracene. The emitter concentration was held constant. Increasing the sensitizer concentration increases the emitter triplet decay rate, increasing the slope of the plot at long times. As higher sensitizer concentration leads to a higher initial triplet concentration, the amount of initial, non-exponential triplet-triplet annihilation also increases.

There are two components to the delayed fluorescence kinetics, a first-order and a second-order component. The second-order component is of greatest importance initially. The amplitude of this component depends on the sensitizer concentration, which determines the initial triplet concentration, $[{}^3E]_0$. At later times, the triplet concentration drops to a level such that the dominant decay term is the first order term, despite the second-order decay giving rise to the signal.

Since I is proportional to $[{}^3E]^2$, the delayed fluorescence kinet-

ics $I(t)$ are^{36–39}

$$\frac{I(t)}{I(0)} = \left(\frac{1 - \beta}{\exp(k_1 t) - \beta} \right)^2 \quad (7)$$

where

$$\beta = \frac{k_2 [^3E]_0}{k_1 + k_2 [^3E]_0} \quad (8)$$

is the initial proportion of triplets which undergo annihilation in a pulsed experiment.

At long times, this expression reduces to

$$\frac{I(t)}{I(0)} \propto \exp(-2k_1 t). \quad (9)$$

In Fig. 4, the decay rate of the emission at long delay times (where the decay straightens out on the logarithmic scale) is bigger for higher concentrations. Fitting the decay curves using Eq. 7, we determine the triplet decay rate k_1 for each sensitizer concentration. The first-order triplet decay rate is faster at high sensitizer concentration.

In Fig. 5, the extracted k_1 is plotted as a function of $[S]$ to generate a Stern-Volmer plot of the form $k_1 = k_1^0 + k_q[S]$. We find that the triplet decay rate increases linearly with sensitizer concentration. The y-intercept is the intrinsic triplet decay rate of the emitter (at that concentration), k_1^0 , and the slope is the additional decay constant caused by the sensitizer concentration. The slope is $k_q = 4.7(4) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ in Pt octaethylporphyrin and diphenylanthracene. As in other second order rate constants, k_q is expected to be proportional to the temperature (295 K) and inversely proportional to the viscosity (0.6 mPa.s).^{42,43}

Similar plots for other sensitizers and emitters are in the ESI[†], and summarized in Table 1. As can be seen, for most experiments, the determined k_q is of the order $10^6 \text{ M}^{-1} \text{ s}^{-1}$, as expected. The Zn octaethylporphyrin/diphenylanthracene couple exhibits a much higher k_q than the other systems. Furthermore, the k_1^0 determined for diphenylanthracene with Zn octaethylporphyrin is 4 times higher than that determined with Pt octaethylporphyrin. Since the intercept occurs at $[S] = 0$, this indicates a discrepancy. Inspection of Figure S18 reveals that the Stern-Volmer plot for the Zn octaethylporphyrin/diphenylanthracene system is sub-linear, which is a feature expected for systems that exhibit incomplete triplet energy transfer due to a small energy gap between the sensitizer and emitter.⁴⁴ In this case the apparent emitter triplet lifetime is determined in part by the triplet lifetime of the sensitizer, and the linear Stern-Volmer model does not apply. Where the triplet energy of the emitter is lower in 9,10-bis(phenylethynyl)anthracene,⁴⁴ the observed quenching constant due to Zn octaethylporphyrin decreases to $1.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, which is still high.

In the supplementary information of Reference 44, Gray et al. reported that the triplet lifetime, as measured by transient absorption, of $10 \mu\text{M}$ 9-phenyl-10-(phenylethynyl)anthracene drops from 2.41 ms to 1.84 ms when the concentration of Pt octaethylporphyrin is increased from $0.5 \mu\text{M}$ to $50 \mu\text{M}$. This corresponds to a quenching rate constant of $2.6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, which is similar

to that observed here for Pt octaethylporphyrin and diphenylanthracene. When Zn octaethylporphyrin was used, the apparent quenching rate constant was $2.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$,⁴⁴ which also accords with the present results.

Keivanidis et al. showed in films of polyfluorene that the phosphorescence lifetime of Pt octaethylporphyrin shortened from 86 to $52 \mu\text{s}$ as its concentration was increased from 0.0004 to 0.15 M.⁴⁵ This corresponds to a bimolecular quenching rate of only $5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, reflecting the high viscosity of the polyfluorene films.

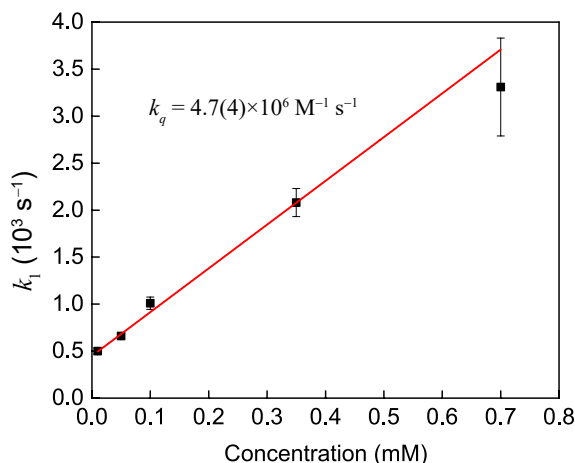


Fig. 5 Stern-Volmer plot of the emitter triplet decay rate as a function of sensitizer concentration. The sensitizer is Pt octaethylporphyrin and the emitter is diphenylanthracene.

The empirical evidence for emitter triplet quenching by sensitizers having been established, naturally one ponders the mechanism of such an interaction. From Table 1, we can tell that the atomic number of the central metal in the sensitizer is not the primary factor in the observed quenching of the emitter triplet by the sensitizer. Indeed, the Zn octaethylporphyrin quenching rate is ten times higher than the Pt octaethylporphyrin, despite Pt having more than twice the nuclear charge. As further confirmation that heavy atom effects^{52–55} alone are not important to our quenching measurements, we added an independent compound containing bromine to an upconverting solution. As shown in Fig. 6, though bromine is a heavier atom than zinc, and the bromine compound is more soluble than octaethylporphyrin, no meaningful change was observed.

Table 1 Photochemical upconversion quenching rate constants. Z_M is the atomic number of the sensitizer central metal, which is the heaviest atom. k_1^0 is the first order triplet decay rate. k_q is second order triplet decay rate as determined from Eq. 5. λ is the excitation wavelength. Color is the color of the upconverted emission (see ESI for spectra[†]). The sensitizers are octaethylporphyrins (OEP), tetraphenyltetraazaporphyrins (TPTB), and a tetrakisquinolalporphyrin (PQ₄).

Sensitizer	Emitter	Z_M	k_1^0 (10^3 s^{-1})	k_q ($10^6 \text{ M}^{-1} \text{ s}^{-1}$)	λ (nm)	Color	Solvent
PtOEP ⁴⁶	diphenylanthracene ⁴⁷	78	0.45 ± 0.03	4.7 ± 0.4	534	blue	toluene
ZnOEP ⁴⁸	diphenylanthracene	30	2.0 ± 0.2	48 ± 7	570	blue	chloroform
ZnOEP	9,10-bis(phenylethynyl)anthracene ⁴⁴	30	3.4 ± 0.4	12 ± 4	570	green	chloroform
PtTPTB ⁴⁹	perylene ⁵⁰	78	0.6 ± 0.1	7 ± 3	613	blue	toluene
PdTPTB ⁵¹	perylene	48	0.49 ± 0.08	7 ± 1	635	blue	toluene
PdPQ ₄ ²⁴	rubrene ²⁴	48	8.9 ± 0.2	0.8 ± 0.7	670	yellow	toluene

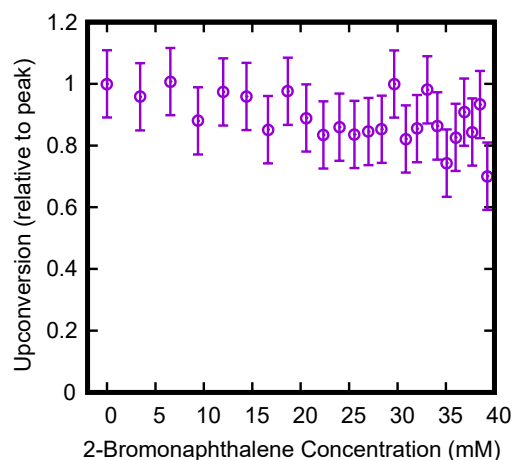


Fig. 6 Photochemical upconversion in Pt octaethylporphyrin and diphenylanthracene as a function of 2-bromonaphthalene concentration. There is little change even though the bromine concentration greatly exceeds the zinc concentration used in Fig. 3. The triplet quenching we observe is not caused by an external heavy atom effect alone.

6 Discussion

The present results have significant implications for solution-based TTA-UC, and furthermore stand as a warning to more elaborate solid states systems. Indeed, any homogeneous system that is limited by the triplet lifetime will suffer from triplet quenching by sensitizer molecules. This statement is true for most systems under one-sun illumination. However, there are several ways that these effects may be circumvented.

In the TTA-OPV device presented by Rand, Scholes and co-workers⁵⁶, sensitized TTA was used to generate singlet excitons which were then harvested by electron transfer. The device comprised α -sexithiophene emitter mixed with platinum tetraphenyltetraazaporphyrin sensitizer in a 50 nm layer. This layer was sandwiched between spacer layers of pure α -sexithiophene, which reduced contact between the site of triplet sensitization and the site of TTA-UC. As noted by the authors, the dilution of triplets in this way can reduce the chance of annihilation. But, if a triplet energy gradient were introduced between a sensitizer layer and an annihilation layer, TTA could occur in a sensitizer-free region, thus ameliorating the quenching effects reported here. This strategy comes at some cost to the upconverted photon energy.

One noteworthy observation is the longevity of triplet states of ligands attached to semiconductor nanocrystal sensitizers.^{57,58} The pyrenecarboxylic acid ligand attached to CdSe nanocrystals

demonstrates a triplet lifetime as long as 50 ms at room temperature. These extremely long lifetimes are surprising given the permanent proximity of the attached sensitizer, but underline that the phenomenon investigated in the present study does not necessarily apply to all classes of sensitizer.

In the solid state device reported by Wu et al., a submonolayer of colloidal nanocrystal sensitizer is held in contact with an 80 nm layer of rubrene emitter.²⁸ Notwithstanding the evidence that triplets are not effectively quenched by nanocrystals, this design also separates the sites of sensitization and annihilation.

The additional triplet decay reported here is clearly detrimental to devices based on photochemical upconversion. Existing strategies for increasing the efficiency of photochemical upconversion, such as increasing the excitation rate of the sensitizer by various means, can effectively mitigate the additional triplet decay. The key is to convert the triplets before they can relax to the ground state. When designing a better photochemical upconverter, the triplet decay rate of an isolated emitter is not sufficient information. The contribution of the sensitizer to triplet storage and emitter performance is also important.

7 Conclusions

We have detected a decay mechanism of the triplet excited state which reduces the performance of photochemical upconversion. The excess triplet decay is triggered by high sensitizer concentration, the resulting second order rate constant being significant in five out of the six photochemical upconversion systems that we tested. In the remaining system, the triplet decay rate of the rubrene emitter is already very high in isolation, potentially owing to its low triplet energy level. The presence or absence of relativistic electrons in the heavy atom in the sensitizer seemingly does not determine how it might modify the emitter's triplet decay rate. Heavy-atom-free upconversion has been demonstrated,⁵⁹ but it is not guaranteed to be free of the presently investigated effects.

8 Experimental

8.1 Conventional steady-state spectra

Absorption spectra were recorded with a Cary 50 Bio UV-Visible spectrometer. Emission spectra were recorded with a Cary Eclipse fluorimeter.

8.2 Photochemical upconversion action spectra

8.2.1 Sample Preparation

Emitter stock solution (15 mM) was prepared in chloroform. Working in ambient air, minimising exposure of the samples to light, weighed quantities of dry sensitizer were dissolved in the stock to yield three full-concentration upconversion solutions with 1.0 mM sensitizer concentration and 15 mM emitter concentration.

Each sample was evaporated by gentle heating, in the dark, overnight, and transferred to a nitrogen glovebox (atmospheric $O_2 < 1$ ppm). Solutions were then re-composed at the original concentration by adding oxygen-free anhydrous toluene. They were sealed against air, and removed for sonication (30 minutes, 60 minutes for Zn octaethylporphyrin, which was less soluble than the other sensitizers), and returned to the glovebox. The samples were left in the low-oxygen environment for 48 hours to re-equilibrate. Dilutions of each solution were made by adding neat toluene.

8.2.2 Optics

The action spectrometer is as previously reported.⁴⁰ For this experiment, the optical bias beam was filtered with a 320 nm long pass filter and a filter which absorbed infrared. Action spectra and Φ_{TTA} were recorded at a range of bias irradiances. Φ_{TTA} at one sun irradiance was calculated by interpolating the data as a function of irradiance. Example action spectra and measurements of Φ_{TTA} as a function of optical bias irradiance are shown in the SI.

8.3 External heavy atom experiment.

To test the external heavy atom effect on photochemical upconversion, we prepared an upconverting solution containing bromine. Two solutions were prepared. The first contained 1 mM diphenylanthracene and 0.3 mM Pt octaethylporphyrin in toluene. The second solution was the same except that it also contained 2-bromonaphthalene.⁶⁰ 2-bromonaphthalene has good transparency in the visible and high solubility.

The first solution was excited using a 535 nm laser diode with a spot radius of 1.3 mm to $1/e^{-2}$ and power 69 W/m^2 . The excitation absorption length was much less than the sample thickness. The photoluminescence was recorded using an Ocean Optics Red Tide spectrometer. Spectra were recorded as the second solution was gradually added to the first solution, increasing the bromine concentration.

Fig. 6 shows the diphenylanthracene fluorescence integrated between 400 nm and 500 nm as a function of 2-bromonaphthalene concentration. The effect of bromine triplet quenching on photochemical upconversion is negligible up to 40 mM. This shows that the triplet quenching effect of Zn octaethylporphyrin at 1 mM on diphenylanthracene cannot be explained by the heavy atom effect of zinc alone. The measurements were performed in an oxygen glove box with < 1 ppm atmospheric oxygen.

8.4 Triplet decay rate measurements

Samples were dissolved in the anhydrous solvent indicated in Table 1 inside a nitrogen glove box. Chloroform was used as the solvent for the Zn octaethylporphyrin experiments because we found it improved solubility. The emitter concentration was 1 mM. Samples and a nitrogen atmosphere were sealed in a 1 mm cuvette with a PTFE tap and removed from the glove box.

The sensitizer Q band was excited using 20 Hz pulses from an OPOTEK Opolette HE 355 LD optical parametric amplifier, pumped by a neodymium doped yttrium aluminum garnet laser. The excitation wavelength is indicated in Table 1. The spot size was 0.4 mm to $1/e^{-2}$ and the pulse energy was 12 J/m^2 . The temperature was 295 K.

The time-dependent photochemical upconversion delayed fluorescence was recorded with a spectrograph and a Princeton Instruments PM4-256f-HR-FG-18-P43-SM electronically gated camera in a front-face geometry. The delayed fluorescence has two kinds of kinetic behaviour: non-exponential triplet-triplet annihilation decay and exponential triplet decay. We were interested in measuring the exponential triplet decay, which is best measured by examining the tail of the time-dependent delayed fluorescence. Therefore the camera exposure was configured to typically saturate at early times and be highly sensitive to the weak signals at later times. Saturated measurements are not displayed.

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Conflict of interest

There are no conflicts to declare.

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