

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231667060>

Kinetic Analysis of Photochemical Upconversion by Triplet–Triplet Annihilation: Beyond Any Spin Statistical Limit

ARTICLE in JOURNAL OF PHYSICAL CHEMISTRY LETTERS · MAY 2010

Impact Factor: 7.46 · DOI: 10.1021/jz100566u

CITATIONS

81

READS

43

8 AUTHORS, INCLUDING:



Yuen Yap Cheng

University of Sydney

30 PUBLICATIONS 619 CITATIONS

SEE PROFILE



Burkhard Fückel

Max Planck Institute for Polymer Research

22 PUBLICATIONS 450 CITATIONS

SEE PROFILE



N.J. Ekins-Daukes

Imperial College London

134 PUBLICATIONS 1,929 CITATIONS

SEE PROFILE



Timothy W Schmidt

University of Sydney

119 PUBLICATIONS 1,463 CITATIONS

SEE PROFILE

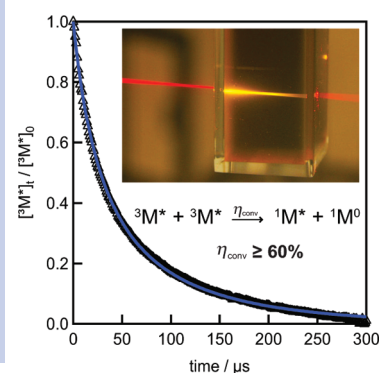
Kinetic Analysis of Photochemical Upconversion by Triplet–Triplet Annihilation: Beyond Any Spin Statistical Limit

Yuen Yap Cheng,[†] Burkhard Fückel,[†] Tony Khoury,[†] Raphaël G. C. R. Clady,[†] Murad J. Y. Tayebjee,[†] N. J. Ekins-Daukes,[‡] Maxwell J. Crossley,[†] and Timothy W. Schmidt^{*,†}

[†]School of Chemistry, The University of Sydney, NSW 2006, Australia, and [‡]Department of Physics and the Grantham Institute for Climate Change, Imperial College, London, UK SW7 2AZ

ABSTRACT Upconversion (UC) via triplet–triplet annihilation (TTA) is a promising concept to improve the energy conversion efficiency of solar cells by harvesting photons below the energy threshold. Here, we present a kinetic study of the delayed fluorescence induced by TTA to explore the maximum efficiency of this process. In our model system we find that more than 60% of the triplet molecules that decay by TTA produce emitters in their first excited singlet state, so that the observed TTA efficiency exceeds 40% at the point of the highest triplet emitter concentration. This result thoroughly disproves any spin-statistical limitation for the annihilation efficiency and thus has crucial consequences for the applicability of an upconverter based on TTA, which are discussed.

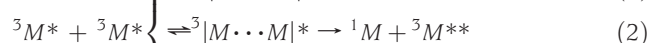
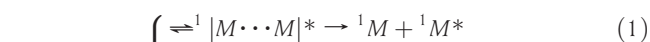
SECTION Kinetics, Spectroscopy



Single threshold photovoltaic devices suffer from their inability to harvest photons below an energy threshold. Upconversion (UC), the combination of two low energy photons into a higher energy photon, can be utilized to address this shortfall.¹ A promising concept is the usage of long-lived triplet states to store low energy quanta.² Low-energy photons are absorbed by sensitizer molecules, which undergo very efficient intersystem crossing (ISC) to their triplet state T_1 upon $S_1 \leftarrow S_0$ excitation. In the next step, the sensitizer molecules transfer their triplet energy to emitter molecules with long triplet lifetimes and large energy gaps between the first triplet state (T_1) and the first excited singlet state (S_1). Upon the encounter of two triplet emitter molecules, triplet–triplet annihilation (TTA) can result in one emitter in its ground state (S_0) and one in its S_1 state (Figure 1). Consequently, delayed fluorescence from the emitter S_1 state is observed.³ When this is at shorter wavelengths than the originally absorbed light, upconversion is manifested. Since this process does not rely on the coherence of the exciting radiation,⁴ it is of interest for improving the energy conversion efficiency of single threshold solar cells. Recently, several new molecular systems have been reported to undergo TTA-UC.^{5–13}

However, to be cost-effective, the upconverter has to attain a certain efficiency. In the case of TTA as the UC process, the underlying mechanism is usually understood in terms of the complex formation between two triplet emitter molecules $^3M^*$.^{14–17} As a consequence of the tensor product of the initial spin states of the molecules, the encounter complex can be of

singlet, triplet, or quintet multiplicity:^{14–17}



Due to the degeneracies of the spin states, the complex formation probabilities are statistically weighted with regard to their multiplicity, that is, in the ratio of 1:3:5, respectively.^{14–17} Only the singlet complex (1 in 9) can dissociate to the S_1 state ($^1M^*$) and yield the desired upconverted fluorescence. An important question is whether these spin statistics limit the efficiency of the TTA-UC process and thereby fundamentally constrain its applicability for solar cells. In the following, we explore this point and define the probability that one S_1 emitter state is formed for each two $^3M^*$ states quenched by TTA (i.e., in the absence of first-order decay processes) as η_{conv} .

The simple spin statistical value of $\eta_{\text{conv}} = 11.1\%$ can be easily revised by taking into account that the quintet encounter complex (eq 3) must dissociate back into the two initial triplet molecules,^{17,18} since a quintet emitter molecule would usually require much higher energies than available. Considering that the triplet encounter complex (eq 2) can produce a higher excited triplet state $^3M^{**}$ (e.g., T_2) that usually undergoes

Received Date: May 3, 2010

Accepted Date: May 18, 2010

Published on Web Date: May 25, 2010

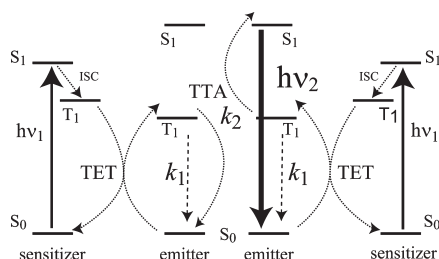
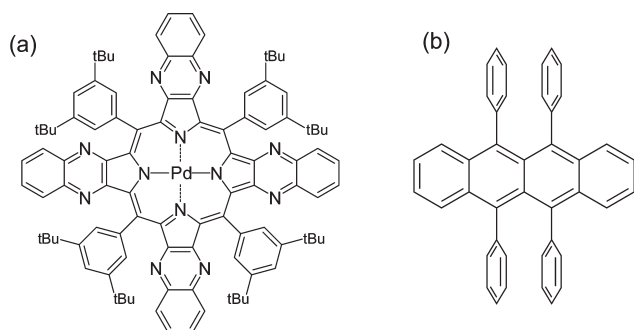


Figure 1. TTA-UC: The sensitizer molecules are excited by low-energy photons $h\nu_1$, undergo fast intersystem crossing (ISC) to the long-lived triplet state T_1 and transfer their energy via triplet energy transfer (TET) to the emitter molecules. Two emitters in the triplet state collide, undergo triplet-triplet annihilation (TTA), and produce one emitter in its singlet state, S_1 . The emitter thereafter fluoresces $h\nu_2$.

Chart 1. Chemical Structures of (a) PQ_4Pd and (b) Rubrene



fast relaxation to $^3M^*$ (T_1), we arrive at a limit of $\eta_{\text{conv}} = 40\%$. By comparison of the prompt and delayed fluorescence of a suitable toluene solution of palladium-porphyrin sensitizer (PQ_4Pd) and rubrene emitter molecules (for structures, see Chart 1; for spectra, see Figure S1, Supporting Information), we have recently shown that indeed annihilation efficiencies $\Phi_{\text{TTA}} > 30\%$ can be obtained,¹⁹ where Φ_{TTA} takes account of any first-order triplet decay, that is, $\Phi_{\text{TTA}} \leq \eta_{\text{conv}}$. If we define f_2 to be the proportion of emitter triplets that decay by second-order means, then $f_2 \times \eta_{\text{conv}} = \Phi_{\text{TTA}}$. As such, when all triplets decay in second order, Φ_{TTA} approaches a limiting value of η_{conv} . Herein, we analyze the kinetics of the latter measurements in order to separate the proportion of emitter triplet decay due to first-order processes, from the decay due to TTA, and thus calculate η_{conv} .

Upon photoexcitation, the sensitizer PQ_4Pd undergoes ISC within a few picoseconds as verified by ultrafast time-resolved measurement of the prompt fluorescence decay of PQ_4Pd (Figure S2). Moreover, a Stern–Volmer plot of the phosphorescence intensity of PQ_4Pd as a function of the rubrene concentration yields a triplet energy transfer (TET) rate of $k_{\text{TET}} = 3.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (Figure S3). Thus, the lifetime of the sensitizer triplet is $\sim 300 \text{ ns}$ at an emitter concentration of 10^{-2} M^{-1} . Hence, within $1 \mu\text{s}$ upon excitation, 95% of the excitons in the sample are present as triplet states of emitter molecules. The forthcoming delayed fluorescence solely originates from S_1 states produced by TTA, that is, its intensity I_F is proportional to the square of the concentration of emitter triplets, $[^3M^*]^2$, in the solution. It occurs on a many microsecond time scale and can therefore be treated independently of the

emitter triplet concentration build-up.²⁰ Thus, for the time-dependence of the concentration of emitter triplet molecules $[^3M^*]$ we can write^{12,15,17}

$$\frac{d\sqrt{I_F(t)}}{dt} \propto \frac{d[^3M^*]_t}{dt} = -k_1[^3M^*]_t - k_2[^3M^*]_t^2 \quad (4)$$

where the first-order decay component k_1 is a combination of the intrinsic phosphorescent and nonradiative decay of the triplet emitter and *quasi* first-order quenching processes. The second-order component, k_2 , originates from the triplet quenching of the TTA process including all bimolecular pathways according to eqs 1–3. The analytical solution to eq 4 is given by¹⁷

$$\frac{[^3M^*]_t}{[^3M^*]_0} = \frac{1 - \beta}{\exp(k_1 t) - \beta} \quad (5)$$

with $\beta = \alpha/(k_1 + \alpha)$, and α being the product of the TTA rate constant and the initial triplet concentration, $\alpha = k_2 [^3M^*]_0$. As pointed out by Bachilo and Weisman, β equates to the initial fraction of decay that occurs through the second-order channel (TTA).¹⁷

Fitting eq 5 to the square-root of the normalized measured delayed fluorescence, we obtain α and k_1 . Examples of the latter fits for various excitation pulse powers are displayed in Figure 2, and the excellent match indicates agreement between theory and data. Obtaining α allows the determination of the proportions of triplets decaying by first- and second-order means, f_1 and f_2 , respectively, which are normalized as $f_1 + f_2 = 1$. That is, by integrating eq 4, the proportion of triplets quenched by the first-order process is given by

$$f_1 = -[^3M^*]_0^{-1} \int_0^\infty k_1 [^3M^*]_t dt = \frac{\beta - 1}{\beta} \ln(1 - \beta) \quad (6)$$

and likewise the proportion of triplets quenched by TTA is

$$\begin{aligned} f_2 &= -[^3M^*]_0^{-1} \int_0^\infty k_2 [^3M^*]_t^2 dt \\ &= 1 - \frac{\beta - 1}{\beta} \ln(1 - \beta) \end{aligned} \quad (7)$$

In solving the integrals in eqs 6 and 7, we used eq 5 to express $[^3M^*]_t$. The values of f_1 and f_2 can now be calculated with the results of the fitting procedure.

The resulting parameters for different excitation energies at fixed rubrene and PQ_4Pd concentrations of $9.9 \times 10^{-3} \text{ M}$ and $4.7 \times 10^{-4} \text{ M}$, respectively, are given in Table 1. With increasing pulse energy, P , the initial concentration of triplet emitter molecules $[^3M^*]_0$ rises, therefore α , β , and f_2 increase. The first-order decay rate, on the other hand, is constant at $k_1 \approx 8.0 \times 10^3 \text{ s}^{-1}$ for the various pulse energies and agrees with values previously reported for the first-order triplet decay constant in various organic solvents including toluene.²¹ We stress that only second-order processes lead to upconverted photons, that is, the proportion of triplets decaying via TTA necessarily produces all of the delayed fluorescence signal. In our previous work we calculated the annihilation efficiency Φ_{TTA} by careful measurement of the respective delayed and

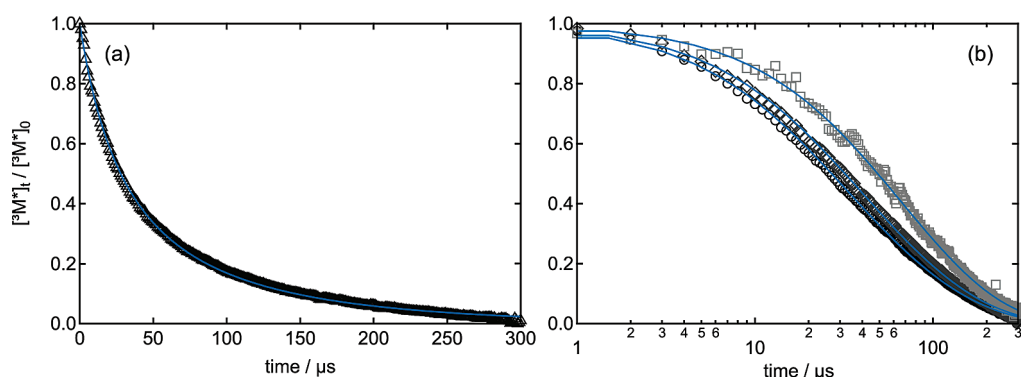


Figure 2. Fits with eq 5 (blue) to the normalized square of the measured delayed fluorescence (symbols) for fixed rubrene and PQ₄Pd concentrations of 9.9×10^{-5} M and 4.7×10^{-4} M, respectively. (a) Pulse energy $P = 10 \mu\text{J}$; (b) for clarity, logarithmic time scale for $P = 15 \mu\text{J}$ (○), $5.0 \mu\text{J}$ (◇), and $1.0 \mu\text{J}$ (□).

Table 1. Parameters^a Obtained from the Fits to the Delayed Fluorescence Signal in Figure 2

$P (\mu\text{J})$	$k_1 (10^5 \text{ s}^{-1})$	$\alpha (10^5 \text{ s}^{-1})$	β	f_2	Φ_{TTA}^b	η_{conv}^c	ϕ_0^d
15	8.1(2)	25.2(4)	0.76(1)	0.55(1)	0.33(3)	0.60(6)	0.46(4)
10	8.1(2)	23.7(5)	0.75(1)	0.53(1)	0.32(3)	0.61(6)	0.45(4)
5	8.0(2)	19.5(4)	0.71(1)	0.49(1)	0.31(3)	0.64(6)	0.45(4)
2.5	8.0(1)	13.9(3)	0.63(1)	0.42(1)	0.27(2)	0.63(6)	0.40(4)
1.25	7.7(2)	9.4(3)	0.55(1)	0.35(2)	0.21(2)	0.60(7)	0.33(4)
1	8.9(3)	7.1(4)	0.44(2)	0.27(4)	0.17(2)	0.63(11)	0.28(5)

^a See text for uncertainty derivation. ^b From ref 19. ^c $\eta_{\text{conv}} = \Phi_{\text{TTA}}/f_2$. ^d $\phi_0 = \beta\eta_{\text{conv}}$.

prompt fluorescence signals, whereby the prompt fluorescence was measured upon direct excitation of the emitter to its S_1 state.¹⁹ Within the kinetic analysis presented herein, we can separate the proportion of triplet emitter molecules that decay via first-order processes and TTA, respectively. Hence, we calculate the efficiency of bimolecular quenching of triplets to yield S_1 emitter states $\eta_{\text{conv}} = \Phi_{\text{TTA}}/f_2$. The values of η_{conv} are constant within the uncertainties at 60%, independent of the employed pulse energy. Through β , we moreover have access to the initial annihilation efficiency $\phi_0 = \beta\eta_{\text{conv}}$ when the emitter triplet concentration is at its peak. For the higher pulse energies, ϕ_0 exceeds 40%. The uncertainties of η_{conv} and ϕ_0 were estimated by an error propagation taking into account the uncertainties of Φ_{TTA} as evaluated in our previous study¹⁹ and twice the standard deviations of k_1 and α obtained by a least-squares fitting procedure as indicated in Table 1.

In Figure 3, mean values $\langle\eta_{\text{conv}}\rangle$ from measurements with various pulse energies are displayed for different concentrations of sensitizer and emitter. η_{conv} is roughly constant within the uncertainty for these different samples, which indicates that it is an intrinsic value of the employed sensitizer/emitter system. The quantity η_{conv} is directly related to the underlying TTA mechanism as depicted in eqs 1–3. Thus, in the investigated system, the conversion efficiency of encounter complexes to excited singlets exceeds the limit calculated assuming that the triplet channel, eq 2 is open, $\eta_{\text{conv}} = 40\%$. Moreover, the initial annihilation efficiency ϕ_0 , that is, the TTA efficiency at the point of the highest triplet emitter concentration, exceeds this limit as well. Up to this point, we have not considered the rate constants of the irreversible dissociation

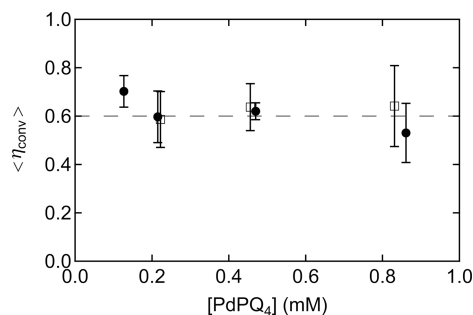


Figure 3. The dependence of the mean of the probability for a pair of triplet rubrene molecules yielding one S_1 emitter state, $\langle\eta_{\text{conv}}\rangle$, on the sensitizer concentration for two different concentrations of rubrene: $[M] = 9 \times 10^{-5}$ M (●) and 4×10^{-5} M (□). The pulse energies $P = 2.5, 5, 10$, and $15 \mu\text{J}$ were taken into account. The error bars display 2 times the standard deviation of the obtained values from the mean. The dashed line is a guide to the eye at $\eta_{\text{conv}} = 0.6$.

of the encounter complexes into a ground state emitter and an excited singlet or a higher excited triplet state molecule for the singlet channel, eq 1, and the triplet channel, respectively. These rates crucially depend on the energies of the product molecules. It is known that the energy of $^3M^{**}$, that is, the rubrene T_2 state, exceeds the energy of its S_1 state by $\sim 700 \text{ cm}^{-1}$ in toluene.²¹ Indeed, for rubrene the energies of the T_1 and T_2 states are about 9300 cm^{-1} and 19200 cm^{-1} above the ground state, respectively.²¹ That is, the formation of a T_2 rubrene state from two T_1 states is endothermic by $\sim 600 \text{ cm}^{-1}$, while the S_1 state is exothermically accessible by 100 cm^{-1} . We attribute this to be the origin for the high

η_{conv} values we found in the above analysis. Hence, we propose that emitter molecules with larger T_2 – S_1 energy gaps than rubrene can yield values for η_{conv} up to unity. Especially when the excitation energy of the emitter T_2 state exceeds double that of its T_1 state, the amount of radiationless decay via the triplet channel is reduced.

η_{conv} sets the ceiling for the annihilation efficiency in the absence of first-order decay processes, thereby laying down the fundamental limit for the efficiency of a TTA-based upconverting module. Assuming that the absorption and ISC process of the sensitizer, as well as the TET to the emitter molecules are much faster than the TTA process, we may treat an upconverter as a simple steady-state system. In contrast to eq 4, under continuous sunlight irradiation, there is an equilibrium of the emitter triplet build-up and decay, i.e., the concentration of emitter molecules in particular states ($[^1M]$, $[^3M^*]$) is constant. Due to the fast ISC in the sensitizer and the rapid TET to the emitter, the build-up of the triplet emitter concentration can be expressed as a first-order behavior depending on the photon flux rate by the sun k_ϕ and the (constant) concentration of ground-state emitter molecules

$$\frac{d[^3M^*]}{dt} = 0 = k_\phi[^1M] - k_1[^3M^*] - k_2[^3M^*]^2 \quad (8)$$

The total concentration of emitter molecules in the sample independent of the respective electronic state, $[M]$, is the sum of $[^1M]$ and $[^3M^*]$, since the fluorescence from $^1M^*$ and relaxation of $^3M^{**}$ to $^3M^*$ is very fast compared to the other processes considered here. We use the fraction of triplet emitter molecules $x = [^3M^*]/[M] = 1 - [^1M]/[M]$ to rewrite eq 8

$$k_\phi[M](1 - x) = k_1[M]x + k_2[M]^2x^2 \quad (9)$$

and calculate the proportion of triplet emitter molecules decaying via TTA,

$$f_2 = \frac{k_2[^3M^*]}{k_1 + k_2[^3M^*]} = \frac{k_2[M]x^2}{k_1x + k_2[M]x^2} \quad (10)$$

Solving eq 9 for x allows determination of f_2 . For modeling purposes, we consider an upconverting material with the following properties: The Q-band of the sensitizer porphyrin employed in the present study absorbs strongly in the wavelength range of 650–700 nm with a maximum molar extinction coefficient of $\epsilon = 1.05 \times 10^6 \text{ M}^{-1} \text{ dm}^{-1}$ (see Figure S1). In combination with the photon flux density ρ in moles of photons $\text{dm}^{-2} \text{ s}^{-1} \text{ nm}^{-1}$ of the AM1.5G standard solar spectrum in this particular wavelength range the sensitizer molecules produce $k_\phi = \int \rho(\lambda)\epsilon'(\lambda) d\lambda = 4.0 \text{ s}^{-1}$, where $\epsilon' = \ln(10)\epsilon$ in units of $\text{M}^{-1} \text{ dm}^{-1}$. The emitter molecule concentration of the upconverter is assumed to be $[M] = 10^{-2} \text{ M}$. We obtain the rubrene TTA rate $k_2 \approx 1.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ in agreement with a previous study²² from $\alpha = k_2[^3M^*]_0$, assuming that the triplet concentration saturates at 50% under ultrafast irradiation. As indicated by the β and f_2 values in 1, the laser pulses with 15 μs saturate the sample. The employed pulse width of $\sim 200 \text{ fs}$ is greater than the usual dephasing time of large organic molecules at room temperature ($\sim 20 \text{ fs}$), and therefore a saturating laser pulse will excite 50% of the molecules in the excitation volume.²³ With these parameters, eq 10 results in

$f_2 = 5.6\%$. Taking into account the conversion efficiency $\eta_{\text{conv}} = 0.6$ extracted herein for our system, little more than 3% of the photons in the range of 650–700 nm of the solar spectrum participate in upconversion and thus can be used for enhancement of a single threshold solar cell. However, the performance can be significantly improved by several steps, e.g., prolonging the emitter triplet lifetime by an order of magnitude would increase f_2 to 67% leading to a maximum of 40% annihilation efficiency. Moreover, a broader sensitizer absorption range and even higher values for η_{conv} can improve the upconverter as well as the concentration of the solar irradiance,²⁴ which will increase the proportion of triplets decaying via TTA. Considering such an improved performance, instantly the applicability of TTA for solar cell improvement is clear. We stress, however, that the practicability of upconverting materials based on TTA for solar cells depends crucially on the photon conversion efficiency η_{conv} . A material limited by spin-statistics, on the other hand, would be fundamentally flawed.

Summarizing, by rigorous kinetic analysis we have extracted the maximal photon conversion efficiency of a TTA system. We have shown that TTA-UC is not inherently limited by spin-statistics *per se*, but that the probability that energy stored in triplet emitter molecules yield fluorescent S_1 states exceeds 60% in our system, and that the TTA efficiency rises above 40% at the point of the highest triplet emitter concentration. Generally, this is an important precondition for the application of TTA-UC for the improvement of solar cells. A consideration of the upconverting properties of the investigated material reveals that this system is on the borderline for application. The search for and design of molecules with favorably ordered electronic states and respective lifetimes will be instrumental to improve the performance of TTA based upconvertors to a suitable state in the near future.

EXPERIMENTAL SECTION

Measurements were performed as previously reported.¹⁹ Toluene solutions of PQ₄Pd and/or rubrene were deaerated through several freeze–pump–thaw cycles. The sample cuvette was illuminated by the tunable output of a TOPAS OPA laser pumped by a Clark MXR femtosecond laser operating at 1 kHz. The $\sim 1 \text{ nm}^2$ fluorescent spot on the front face of the cuvette was entirely imaged, with a lens, through the slits of a spectrograph and detected with an iCCD camera (Acton/Princeton). The kinetics of delayed fluorescence were measured in 1 μs slices, from 1 to 300 μs delay. Fitting of the delayed fluorescence signal was performed with IgorPro 6.1 (Wavemetrics).

SUPPORTING INFORMATION AVAILABLE Absorption and emission spectra of the employed compounds; the fluorescence decay of PQ₄Pd; a Stern–Volmer plot of the quenching of the PQ₄Pd phosphorescence in dependence of the rubrene concentration. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

AUTHOR INFORMATION

Corresponding Author:

*To whom correspondence should be addressed. E-mail: timothy.schmidt@sydney.edu.au. Phone: +61 2 9351 2781. Fax: +61 2 9351 3329.

ACKNOWLEDGMENT Y.Y.C. acknowledges The University of Sydney for a Gritton Fellowship. M.J.Y.T. acknowledges the receipt of an Australian Postgraduate Award. B.F. acknowledges the Alexander von Humboldt foundation for a Feodor Lynen fellowship. This work was supported by The University of Sydney (2008-00511 Efficient upconversion for photovoltaic devices) and the Australian Research Council (LE0668257).

REFERENCES

- Trupke, T.; Green, M. A.; Würfel, P. Improving Solar Cell Efficiencies by Up-Conversion of Sub-band-gap Light. *J. Appl. Phys.* **2002**, *92*, 4117–4122.
- Ekins-Daukes, N. J.; Schmidt, T. W. A Molecular Approach to the Intermediate Band Solar Cell: The Symmetric Case. *Appl. Phys. Lett.* **2008**, *93*, 063507:1–3.
- Sternlicht, H.; Robinson, G. W.; Nieman, G. C. Triplet–Triplet Annihilation and Delayed Fluorescence in Molecular Aggregates. *J. Chem. Phys.* **1963**, *38*, 1326–1335.
- Baluschev, S.; Miteva, T.; Yakutkin, V.; Nelles, G.; Yasuda, A.; Wegner, G. Up-Conversion Fluorescence: Noncoherent Excitation by Sunlight. *Phys. Rev. Lett.* **2006**, *97*, 143903:1–3.
- Kozlov, D. V.; Castellano, F. N. Anti-Stokes Delayed Fluorescence from Metal–Organic Bichromophores. *Chem. Commun.* **2004**, *24*, 2860–2861.
- Laquai, F.; Wegner, G.; Im, C.; Büsing, A.; Heun, S. Efficient Upconversion Fluorescence in a Blue-Emitting Spirobifluorene–Anthracene Copolymer Doped with Low Concentrations of Pt(II)octaethylporphyrin. *J. Chem. Phys.* **2005**, *123*, 074902:1–6.
- Baluschev, S.; Yakutkin, V.; Miteva, T.; Avlasevich, Y.; Chernov, S.; Aleshchenkov, S.; Nelles, G.; Cheprakov, A.; Yasuda, A.; Müllen, K. e. a. Blue-Green Up-Conversion: Noncoherent Excitation by NIR Light. *Angew. Chem., Int. Ed.* **2007**, *46*, 7693–7696.
- Baluschev, S.; Yakutkin, V.; Wegner, G.; Miteva, T.; Nelles, G.; Yasuda, A.; Chernov, S.; Aleshchenkov, S.; Cheprakov, A. Upconversion with Ultrabroad Excitation Band: Simultaneous Use of Two Sensitizers. *Appl. Phys. Lett.* **2007**, *90*, 181103:1–3.
- Singh-Rachford, T.; Castellano, F. Pd(II) Phthalocyanine-Sensitized Triplet–Triplet Annihilation from Rubrene. *J. Phys. Chem. A* **2008**, *112*, 3550–3556.
- Singh-Rachford, T. N.; Haefele, A.; Ziessel, R.; Castellano, F. N. Boron Dipyrromethene Chromophores: Next Generation Triplet Acceptors/Annihilators for Low Power Upconversion Schemes. *J. Am. Chem. Soc.* **2008**, *130*, 16164–16165.
- Monguzzi, A.; Tubino, R.; Meinardi, F. Multicomponent Polymeric Film for Red to Green Low Power Sensitized Up-Conversion. *J. Phys. Chem. A* **2009**, *113*, 1171–1174.
- Singh-Rachford, T. N.; Castellano, F. N. Low Power Visible-to-UV Upconversion. *J. Phys. Chem. A* **2009**, *113*, 5912–5917.
- Singh-Rachford, T. N.; Castellano, F. N. Triplet Sensitized Red-to-Blue Photon Upconversion. *J. Phys. Chem. Lett.* **2010**, *1*, 195–200.
- Charlton, J. L.; Dabestani, R.; Saltiel, J. Role of Triplet Triplet Annihilation in Anthracene Dimerization. *J. Am. Chem. Soc.* **1983**, *105*, 3473–3476.
- Saltiel, J.; Atwater, B. *Advances in Photochemistry*; Wiley: New York, 1988.
- McLean, A. J.; Truscott, T. G. Efficiency of Triplet-Photosensitized Singlet Oxygen Generation in Benzene. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 2671–2672.
- Bachilo, S. M.; Weisman, R. B. Determination of Triplet Quantum Yields from Triplet–Triplet Annihilation Fluorescence. *J. Phys. Chem. A* **2000**, *104*, 7711–7714.
- Levin, P. P.; Costa, S. M. B.; Nunes, T. G.; Ferreira, L. F. V.; Ilharco, L. M.; do Rego, A. M. B. Kinetics of Triplet–Triplet Annihilation of Tetraphenylporphyrin in Liquid and Frozen Films of Decanol on the External Surface of Zeolite. Fast Probe Diffusion in Monolayers and Polycrystals. *J. Phys. Chem. A* **2003**, *107*, 328–336.
- Cheng, Y. Y.; Khoury, T.; Clady, R. G. C. R.; Tayebjee, M. J. Y.; Ekins-Daukes, N. J.; Crossley, M. J.; Schmidt, T. W. On the Efficiency Limit of Triplet–Triplet Annihilation for Photochemical Upconversion. *Phys. Chem. Chem. Phys.* **2010**, *12*, 66–71.
- Auckett, J. E.; Cheng, Y. Y.; Khoury, T.; Clady, R. G. C. R.; Ekins-Daukes, N. J.; Crossley, M. J.; Schmidt, T. W. Efficient Up-Conversion by Triplet–Triplet Annihilation. *J. Phys. Conf. Ser.* **2009**, *185*, 012002:1–4.
- Lewitzka, F.; Löhmansröben, H. G. Investigation of Triplet Tetracene and Triplet Rubrene in Solution. *Z. Phys. Chem. Neue Folge* **1986**, *150*, 69–86.
- Herkstroeter, W. G.; Merkel, P. B. The Triplet State Energies of Rubrene and Diphenylisobenzofuran. *J. Photochem.* **1981**, *16*, 331–341.
- van Dijk, E. M. H. P.; Hernando, J.; Garcia-Lopez, J. J.; Crego-Calama, M.; Reinhoudt, D. N.; Kuipers, L.; Garcia-Parajo, M. F.; van Hulst, N. F. Single-Molecule Pump–Probe Detection Resolves Ultrafast Pathways in Individual and Coupled Quantum Systems. *Phys. Rev. Lett.* **2005**, *94*, 078302:1–4.
- Currie, M. J.; Mapel, J. K.; Heidel, T. D.; Goffri, S.; Baldo, M. A. High-Efficiency Organic Solar Concentrators for Photovoltaics. *Science* **2008**, *321*, 226–228.