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Mechanisms of Low-Power Noncoherent Photon Upconversion in Metalloporphyrin−Organic Blue Emitter Systems in Solution

Sunish K. Sugunan,[†] Umakanta Tripathy,[†] Sophie M. K. Brunet,[‡] Matthew F. Paige,*,[†] and Ronald P. Steer*,[†]

Department of Chemistry and Saskatchewan Structural Sciences Centre, University of Saskatchewan Saskatoon, Saskatchewan S7N 5C9, Canada

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The mechanisms of noncoherent photon upconversion that involve triplet−triplet annihilation (TTA) in solution have been investigated for two model systems. ZnTPP (*meso*-tetraphenylporphine zinc) is used as the model visible light-absorbing metalloporphyrin because its S_1 fluorescence intensity can be used to monitor the initial rate of porphyrin triplet state production and because its S_2 fluorescence intensity can be used as a direct measure of the rate of porphyrin TTA. When perylene, which has a triplet energy lower than that of ZnTPP, is added as a signaling blue emitter (BE), the mechanism of photon upconversion involves triplet energy transfer from the porphyrin to the BE followed by TTA in the BE to form the fluorescent perylene S_1 state. The kinetics of this process have been characterized and are unremarkable. When coumarin 343 (C343), which has photophysical properties similar to those of perylene except that it has a much higher triplet energy than ZnTPP, is added as the signaling BE, emission from the ZnTPP S_2 state is quenched and fluorescence from the C343 grows in. Contrary to previous suggestions, the mechanism of photon upconversion in this system does not involve singlet energy transfer from the porphyrin S_2 state to the BE. Instead, ground-state C343 complexes with the ZnTPP triplet to form a triplet exciplex, which then undergoes TTA with a second ZnTPP triplet to give the fluorescent state of the BE in a three-center process.

Introduction

Electronic excited state annihilation processes have received considerable attention recently due to the prospect of using them in photon upconversion schemes.[1−6] The ability to generate fluorescent electronic states with energies higher than those of the photon absorber finds application in photon-driven molecular logic devices,[1] in various kinds of photonic sensors,[2] in the design and construction of single photon sources[3] and in solar energy harvesting schemes.[4−6] The latter application is particularly attractive because noncoherent photon upconversion offers a novel means of improving the overall efficiency of solar energy utilization in organic dye-sensitized solar cells (DSSCs).[7]

Among the various excited state annihilation processes reported to date,[8] triplet−triplet annihilation (TTA),

$$2T_1 \rightarrow S_n\,(n \geq 1) + S_0 \tag{1}$$

appears to be attractive for practical implementation in upconversion devices.[4] TTA has been observed in both fluid and solid media and in thin films[4−6] and offers the prospect of good excited singlet state yields at low excitation powers due to the long lifetimes of the triplet states that act as the molecular energy storage units in this process. Sensitizers for use in DSSCs employing noncoherent photon upconversion should absorb strongly in the red and near-infrared where the solar spectrum is photon-rich but where one-photon actuated dye-sensitized solar cells exhibit a falloff in efficiency.[7,9]

TTA was first reported many decades ago,[10] and the kinetics of the process whereby delayed fluorescence from the lowest excited singlet state (S_n ($n = 1$)) of a fluorophore is produced by TTA of its lowest triplet state has been well established.[11] TTA producing higher excited singlet states, S_n ($n > 1$), can in principle capture a greater fraction of the absorbed photon energy in the excited singlet product and is thus of considerable importance. However, these TTA processes are rarer[12] and have not been as well-characterized. TTA producing a fluorescent S_2 state was first observed in the metalloporphyrins (potential sensitizers in DSSCs) by Tsvirko, Stel'makh, and co-workers,[13] has been kinetically characterized in the TTA of aromatic thiones,[14] and has recently been proposed to be an element in the noncoherent photon upconversion and energy transfer schemes for solar energy capture.[4−6]

Baluschev and co-workers[4] have proposed two schemes by which TTA can effect noncoherent photon upconversion following absorption of mid-visible to red light by metalloporphyrins (MP) and subsequent sensitization of fluorescence from an added "blue emitter" (BE) in deoxygenated systems. The more efficient route involves triplet electronic energy transfer (TEET) from the triplet state of the metalloporphyrin to a lower-lying triplet state of the BE, followed by TTA in the BE:

$$S_0(\mathrm{MP}) + h\nu_{\mathrm{vis}} \rightarrow S_1(\mathrm{MP}) \tag{2}$$

$$S_1(\mathrm{MP}) \rightarrow T_1(\mathrm{MP})\ (\eta_{\mathrm{isc}} \approx 1) \tag{3}$$

$$T_1(\mathrm{MP}) + S_0(\mathrm{BE}) \rightarrow T_1(\mathrm{BE}) + S_0(\mathrm{MP}) \tag{4}$$

$$2T_1(\mathrm{BE}) \rightarrow S_1(\mathrm{BE}) + S_0(\mathrm{BE}) \tag{5}$$

$$S_1(\mathrm{BE}) \rightarrow S_0(\mathrm{BE}) + h\nu_{\mathrm{blue}} \tag{6}$$

Evidence of TTA and energy transfer is obtained by observing the fluorescence from the BE, step 6, and by following the temporal behavior of the intermediate triplet states.

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* To whom correspondence should be addressed. E-mail addresses: ron.steer@usask.ca; matthew.paige@usask.ca. Phone: (306) 966-4667. Fax: (306) 966-4730.

[†] Department of Chemistry.

[‡] Saskatchewan Structural Sciences Centre.

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When the BE has a triplet energy substantially higher than that of the porphyrin sensitizer, Baluschev et al.[4d,e] propose a second mechanism that is less efficient, involving singlet electronic energy transfer (SEET) from a higher excited singlet state of the metalloporphyrin produced by TTA, that is, steps 2 and 3 followed by

$$2T_1(MP) \rightarrow S_2(MP) + S_0(MP) \tag{7}$$

$$S_2(MP) + S_0(BE) \rightarrow S_0(MP) + S_1(BE) \tag{8}$$

and again observing fluorescence from the BE, step 6.

The mechanisms proposed by Baluschev et al.[4] are somewhat controversial.[15] The SEET mechanism, step 8 above, relies on an unusual energy transfer from a highly excited singlet state of the metalloporphyrin. Such energy transfers have been reported in porphyrin aggregates[16] and in tethered azulene–porphyrin dyads[17] in which the donor is relatively long-lived. However, step 8 in this mechanism would be impossibly inefficient if it were to occur by a standard FRET mechanism because the second excited singlet states of β-octaethylporphine platinum (PtOEP) and palladium (PdOEP) used in their experiments are nonfluorescent[18] and must therefore be very short-lived ($\ll$1 ps). Moreover, Baluschev et al.[4] do not propose heteromolecular TTA involving annihilation of a triplet of the porphyrin with a triplet of the BE, and they and others have not taken into account aggregation phenomena that are known[19] to be important in porphyrin systems, both in solution and in the solid phase.

We have studied in detail the excited state dynamics and photophysics of d^0 and d^{10} metalloporphyrins such as *meso*-tetraphenylporphrine zinc (ZnTPP) that fluoresce from their S_2 states.[20] Soret band, $S_2 \rightarrow S_0$, emission can act as a useful metric for TTA and SEET of the type proposed by Baluschev et al.,[4] and the use of metalloporphyrins in which the metals have filled d shells also eliminates the possibility of involving charge transfer states[21] in the photon upconversion mechanism. We now use the information gained from our previous studies together with the results of new experiments to examine the processes of metalloporphyrin TTA and SEET in solution with the object of clarifying the mechanisms of noncoherent photon upconversion in these systems.

Experimental Section

Materials. ZnTPP (Frontier Scientific) and blue emitters perylene (P) and coumarin 343 (C343) (both from Sigma-Aldrich) were used as received. Absorption, fluorescence emission, and excitation spectra of the starting materials in dilute solution were identical to those published previously[20,22,23] and showed that there were no fluorescent impurities present in the samples. All the solvents (Sigma-Aldrich) were of HPLC grade ($\geq$99.9% purity) and were dried using appropriate molecular sieves. Sample preparations for experiments involving pyridine and DMF were carried out in a dry nitrogen environment in a glovebox to avoid contamination by water vapor. All samples for the TTA and associated energy transfer experiments were degassed by at least four freeze–pump–thaw cycles on a grease-free high vacuum line.

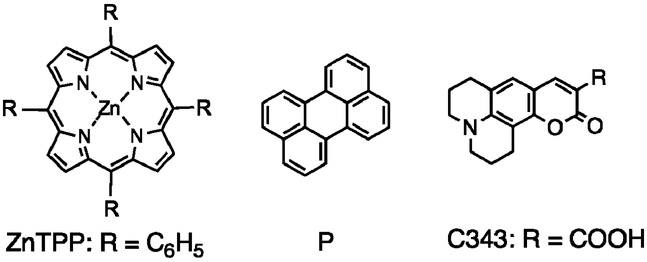
Instrumentation and Methods. Steady-state absorption measurements were taken using a Varian-Cary 500 spectrophotometer and routine fluorescence emission and emission excitation measurements were carried out using a PTI Quantamaster spectrofluorometer, both at the same spectral bandwidth (2.0 nm).

The TTA experiments were carried out using a modified Jobin-Yvon Spex Fluorolog spectrofluorometer equipped with a double grating monochromator and a cooled single-photon-counting detector on the emission side. The sample chamber was modified to accommodate excitation by a low-power (<30 mW), frequency-doubled cw Nd:YAG laser (WSTech, TECGL-30) at 532 nm operating in TEM_{00}. For most experiments, front-face illumination of a sealed triangular cell was employed to provide partial relief from problems of fluorescence reabsorption. A calibrated 10-step, graded neutral density filter (Edmund Optics) was used to attenuate the power of the incident laser beam, and a 532 nm notch filter in the emission path was used to reduce scattered excitation light in some experiments. Power densities (or irradiances in W cm^{-2}) were obtained by measuring the total laser power transmitted through the neutral density filter and calculating the 1/e spot size from the divergence of the laser beam, assuming pure TEM_{00} mode structure. All the emission spectra were corrected for the wavelength-dependent response of the detector using the correction files provided by the manufacturer. In addition, when different emission slit widths were employed in different regions of the spectrum in order to operate the detector within its linear response range, the overall fluorescence intensities were normalized to a fixed emission bandwidth.

The spectra themselves were corrected for fluorescence reabsorption by the emitting species, a problem that was extreme at high added BE concentrations. When these corrections were made for front-face illumination of the triangular cell, using a 45° emission-to-excitation fluorescence collection angle, the method previously reported by Lopez[24] was employed. Correction procedures are described fully in the Supporting Information.

Results and Discussion

The mechanisms of photon upconversion in solution have been investigated using two model absorber/blue emitter systems, *meso*-tetraphenylporphine zinc (ZnTPP) plus perylene (P) and ZnTPP plus coumarin 343 (C343). Their structures are shown below.



ZnTPP: R = C_6H_5 P C343: R = COOH

The absorption spectra of ZnTPP and the two BEs employed in this study are similar to those previously published[20,22,23] and are reproduced in the Supporting Information for this paper. Only ZnTPP is a significant absorber of the 532 nm (18 797 cm^{-1}) excitation light used in the TTA experiments; both BEs have molar absorptivities approaching zero at this wavelength. At the typical ZnTPP concentration used in the TTA experiments, 0.10 mM, some aggregation of ground-state porphyrin is expected,[19] and this is observed as a slight broadening of the absorption spectrum. Nevertheless, in benzene solution this phenomenon is minimized (relative to the greater aggregation found in poor solvents such as cycloalkanes[20]) and does not

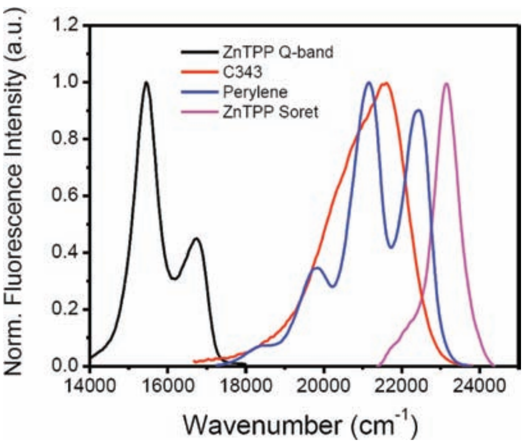


Figure 1. Separately normalized, directly excited fluorescence spectra of ZnTPP, C343, and perylene. The sample solutions were all of the same concentration (1.0×10^{-4} M) in benzene. Perylene was excited at the wavelength of its absorption maximum at 442 nm (22 600 cm^{-1}). C343 and ZnTPP were excited at 410 nm (24 400 cm^{-1}) to the blue of the absorption maxima to minimize scattered light corrections. Fluorescence was collected with a PTI spectrophotometer with bandpasses of 2.0 nm on both the excitation and emission monochromators.

significantly affect the results of the TTA and energy transfer experiments (*vide infra*).

The prompt, corrected emission spectra of benzene solutions of ZnTPP and of the two blue emitters, C343 and P, employed in this study are shown in Figure 1. These spectra were obtained by means of one-photon excitation of the fluorophores at or near their respective absorption maxima at concentrations lying within the range of concentrations employed in the TTA and emission quenching measurements undertaken in later experiments. These spectra do exhibit some evidence of minor solute aggregation (broadening and minor shifts in peak maxima), but are nonetheless similar to the spectra taken in dilute solution.[20,22,23] Note in particular that the Soret band and Q-band emission spectra of the ZnTPP absorber bracket the emission spectra of the two organic blue emitters and that contamination of the emission spectra of the blue emitters by the weak fluorescence of the ZnTPP is expected to be minor. Note also, however, that in mixed ZnTPP−BE experiments absorption of the blue emitters will cause considerable difficulty in extracting the true Soret emission intensities of ZnTPP in the violet region and that reabsorption of BE fluorescence by the BEs themselves will also be significant. For these reasons, front-face illumination of the ZnTPP−BE systems in a triangular cell and a specialized reabsorption correction procedure were employed for most experiments (see Experimental Section).

The spectra resulting from 532 nm excitation of 0.10 mM ZnTPP solutions in several degassed coordinating and noncoordinating solvents at a fixed excitation power are shown in Figure 2. Note that the emission intensities in these spectra have been corrected to a common absorbance at the excitation wavelength; the observed differences are solvent, but not concentration, dependent. Excitation at 532 nm in the Q absorption band of the metalloporphyrin produces relatively strong $S_1(1^1E_u) \rightarrow S_0(^1A_{1g})$ fluorescence in the red region of the spectrum with intensities that are somewhat solvent dependent, as has been frequently reported previously.[20] Note, however, that the intensity of the $S_2(2^1E_u) \rightarrow S_0(^1A_{1g})$ fluorescence in the violet region of the spectrum resulting from homomolecular TTA of the porphyrin triplet (1^3E_u) is highly solvent dependent and is strongly suppressed in coordinating solvents such as pyridine, DMF, and acetonitrile. Note also that in the noncoordinating solvents, the spectrum of the S_2 fluorescence is slightly red-shifted (by up to 300 cm^{-1}) compared with that observed on one-photon excitation of dilute solutions of ZnTPP in the same solvent. The latter red-shift has been previously noted by Tsvirko and Stel'makh,[13] who reasonably attributed the effect to perturbation of the emitting $S_2(2^1E_u)$ species by a second (ground-state) ZnTPP molecule. The perturbation is only seen in the TTA delayed fluorescence spectrum because the radiative species is very short-lived (approximately picosecond)[20] and emits before the second ZnTPP molecule of the TTA pair has had a chance to diffuse away.

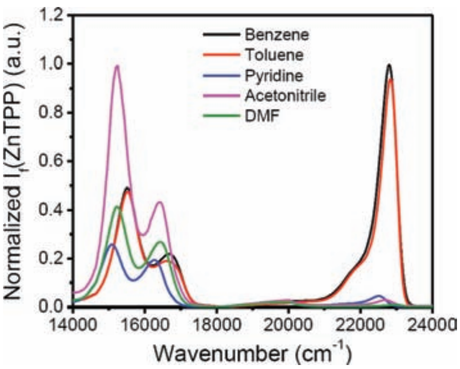


Figure 2. Prompt S_1 fluorescence and delayed S_2 fluorescence obtained from front-face excitation of 1.0×10^{-4} M ZnTPP in degassed noncoordinating solvents (benzene and toluene) and coordinating solvents (pyridine, acetonitrile, and *N*,*N*-dimethylformamide) with a 532 nm (18 797 cm^{-1}) cw laser at an incident power density of 0.28 W/cm^2 and a fluorometer with a 3.6 nm emission bandpass.

TTA in solution occurs primarily as a result of short-range electron exchange interactions between pairs of triplet states whose bimolecular encounters are diffusion controlled. The relative intensities of the Soret band emission produced by TTA in various degassed solvents can therefore be analyzed in terms of Dexter's theory of triplet energy transfer,[6a,25] allowing for differences in diffusion rates where required. Here, we assign the solvent dependence of the TTA rate primarily to the increase in the average distance between the two triplets in the encounter pairs caused by axial noncovalent coordination in solvents such as pyridine compared with noncoordinating solvents such as benzene. In fact the involvement of axially coordinated solvent species in suppressing TTA may be followed quantitatively by titrating pyridine into benzene solutions of ZnTPP, as shown in Figure 2 in the Supporting Information. The addition of small incremental amounts of pyridine causes both a diminution in the intensity of the porphyrin's delayed fluorescence, and also a shift in the spectrum of this fluorescence to longer wavelengths. The bathochromic shift of the emission in coordinating solvents is also seen when the S_2 fluorescence of ZnTPP is excited by one-photon absorption in its Soret band and has been attributed to axial coordination at zinc.[26]

The simplest realistic model[6a] based on Dexter's theory yields eq 9 to describe the ratio of the rate of TTA in a noncoordinating solvent to that in a coordinating solvent:

$$R_{\mathrm{calc}} = \frac{k_{\mathrm{NC}}}{k_{\mathrm{C}}} = \frac{A_{\mathrm{NC}} \exp(-2R_{\mathrm{NC}}/L)}{A_{\mathrm{C}} \exp(-2R_{\mathrm{C}}/L)} \approx \frac{\eta_{\mathrm{C}}}{\eta_{\mathrm{NC}}} \exp\{2(R_{\mathrm{C}} - R_{\mathrm{NC}})/L\} \quad (9)$$

Here R_{C} and R_{NC} are the encounter distances in the coordinating and noncoordinating solvents, respectively, and $L = 0.48$ nm

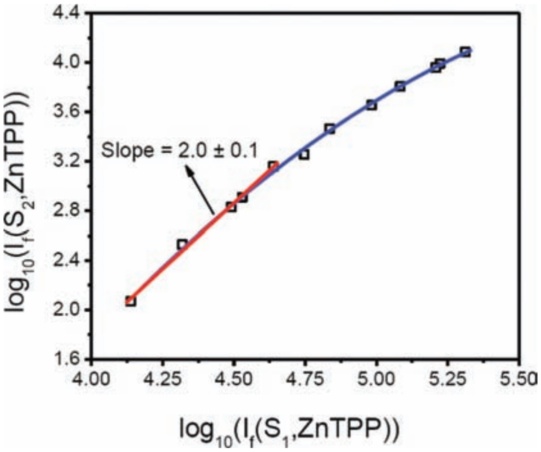


Figure 3. Plot of $\log_{10}$ of delayed S_2 fluorescence intensity versus $\log_{10}$ of prompt S_1 fluorescence intensity as a function of increasing laser power using a 532 nm cw laser and front-face excitation of 1.0×10^{-4} M ZnTPP in degassed benzene.

is the effective Bohr radius[27] of the metalloporphyrin. The pre-exponential factors, A_{NC} and A_C in eq 9 include both the overlap integral and the diffusion rate constants. The diffusion constants vary inversely with the solvent viscosity, η, and we assume that the overlap integrals are identical for ZnTPP in both coordinating and noncoordinating solvents. Semiempirical AM1 calculations were employed to estimate R_C and R_{NC} from the Zn···Zn distances in encounter pairs having a variety of possible geometries. The differences $R_C - R_{NC}$ are associated with axial binding of the coordinating solvent molecule to ZnTPP and range from 0.98 to 1.14 nm for pyridine. Inserting these values in eq 9 then yields calculated estimates of R_{calc} that fall in the range of 12−24 for the case of benzene and pyridine solvents (for which the ratio of the diffusion coefficients is $\eta_C/\eta_{NC} = 1.5$). This range is to be compared with a measured ratio of TTA fluorescence intensities of 22 for the same solvent pair (Figure 2). The agreement between the observed and calculated values of R is reasonable considering the uncertainty in L, the errors attending the computed geometries, and the crude approximation involved in equating R_C and R_{NC} to the Zn···Zn distances in the encounter pairs. We proceed on the basis that TTA in ZnTPP triplets occurs by a Dexter, electron exchange mechanism and that the rate of triplet−triplet encounters is diffusion limited.

The quantum efficiency of intersystem crossing from the initially populated S_1 state of ZnTPP to its lowest triplet (T_1) state is high (various measurements quote $\eta_{isc} \approx 0.9$).[28] Nevertheless, the S_1 fluorescence intensity of ZnTPP is readily measurable; the quantum yield, $\phi_f(S_1)$, is 0.04 in benzene[28,29] at room temperature. Thus the intensity of Q-band fluorescence can serve as a relative measure of the average initial concentration of T_1 under a variety of excitation conditions, that is, $I_f(S_1,\text{ZnTPP}) \propto [T_1]$. The intensity of S_2 emission resulting from TTA in ZnTPP, $I_f(S_2,\text{ZnTPP})$, is clearly proportional to $[T_1]^2$, so a double logarithmic plot such as Figure 3 should reveal information about the excitation power dependence of the TTA process. Note that the slope of this double logarithmic plot is 2.0 ± 0.1 in the low excitation power range, as required if no process consumes a significant fraction of incident photons without producing triplet states. At higher excitation powers, the slope of the tangent to the curve diminishes, indicating that photon-wasting processes such as triplet−triplet absorption may be occurring. In ZnTPP, $T_1 \rightarrow T_n$ absorptions exhibit large oscillator strengths in the visible region of the spectrum[30] and increase in importance with increasing $[T_1]$, resulting in photon absorption without the concomitant production of triplet states. All subsequent experiments, other than excitation power dependence measurements themselves, were undertaken at excitation power densities in the upper end of the low power density range of Figure 3, at ca. 0.28 W cm^{-2}, where the slope of the tangent to the curve in Figure 3 is slightly less than 2.0.

TABLE 1: Spectroscopic and Photophysical Data for Compounds Used in This Study

	ZnTPP	Perylene	Coumarin 343	references
$E(S_2)$ (cm^{-1})	23580			20
$E(S_1)$ (cm^{-1})	16865	22700	22600	20, 22, 23
$E(T_1)$ (cm^{-1})	12850	12371	16581	30−32
$\tau(S_1)$ (ns)	2.0	5.5	4.0	32, 22, 23
$\tau(T_1)$ (ms)	1.2, 0.6	1.1, 0.3		(34, 35),(36, 22)
η_{isc}	0.9	0.01		28, 22
ϕ_{f,S_2}	1.1×10^{-3}			20
ϕ_{f,S_1}	0.04	0.98	0.63	29, 22, 37

Two BEs, perylene (P) and coumarin 343 (C343), were selected as energy acceptors to test the mechanism(s) of TTA and energy transfer in deoxygenated benzene solutions of ZnTPP. The spectroscopic and photophysical data that characterize the donor and acceptor molecules are collected in Table 1. Both of these BEs have similar S_1 energies that lie slightly lower than the S_2 energy of ZnTPP (cf. absorption and emission spectra), and both have similar S_1 lifetimes and radiative transition rates. However, P has a T_1 energy lower than that of ZnTPP, whereas C343 has a T_1 energy significantly higher than that of ZnTPP. In deoxygenated fluid solution at room temperature, the lifetime of triplet P is similar to that of ZnTPP. The lifetime of triplet C343 has not been measured, but because this compound is used as an efficient laser dye, it must have both a short triplet lifetime and a small S_1-T_1 intersystem crossing yield. Neither BE absorbs significantly at 532 nm. In aggregate, the data in Table 1 illustrate that the two BEs are excellent probes for uncovering any differences in the photon upconversion mechanism in the two model systems.

The results of experiments in which the fluorescence spectra excited at 532 nm were measured as a function of increasing concentrations of P in a 0.10 mM solution of ZnTPP in benzene are shown in Figure 4. These results are largely unremarkable, and simply exhibit the expected increase in $P(S_1)$ fluorescence intensity with increasing [P]. The small amount of ZnTPP S_2 emission from TTA is completely quenched at low perylene concentrations, and no excimer emission from perylene is observed. The mechanism is clearly one of TEET followed by TTA in the acceptor, steps 2−6, as described many times in the literature. Overlapping of the very strong S_1 emission from P with the weak S_2 emission from ZnTPP prevented quantitative measurement of the S_2 emission quenching kinetics under steady-state conditions. S_1-S_0 fluorescence reabsorption in the perylene also distorted the perylene emission spectrum in its short-wavelength segment, as can readily be seen in Figure 4. Nevertheless, the most intense emission feature at 22 780 cm^{-1} could be corrected accurately at perylene concentrations up to 1.0 mM using the technique described in the Experimental Section. Above this concentration, the correction factors became very large and the apparent decrease in fluorescence intensity could not be assigned unambiguously to concentration quenching of the perylene excited states by ground-state P. The details of the correction procedure are given in the Supporting Information for this paper.

The corrected intensities were used to plot Figure 5A,B, which shows how the perylene fluorescence intensities vary with power

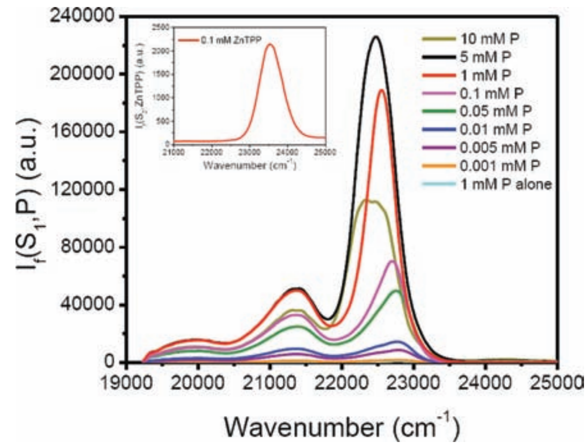


Figure 4. Upconverted S_1 fluorescence obtained from various concentrations of perylene in a solution containing 1.0×10^{-4} M ZnTPP in degassed benzene. Samples were excited in front-face geometry with a 532 nm (18 797 cm^{-1}) cw laser at a power density of 0.28 W cm^{-2} and a spectrometer with a 1.0 nm emission bandpass. The spectra were corrected for the detector response as a function of wavelength and for reabsorption by perylene, which is large in the >22 000 cm^{-1} region. The inset shows the corrected delayed S_2 emission spectrum obtained from 1.0×10^{-4} M ZnTPP in benzene in the absence of perylene under the same experimental conditions.

of the excitation laser at a fixed perylene concentration and with perylene concentration at fixed laser power. Both double logarithmic plots are nonlinear. The former is mildly nonlinear and exhibits a tangential slope at low power approaching 2, confirming that the perylene S_1 emission arises from photon upconversion by TEET followed by TTA in the perylene triplet. The latter shows a high degree of nonlinearity and exhibits a tangential slope of ca. 1 at the lowest perylene concentrations employed but reaches an asymptote at high perylene concentrations. The latter behavior is consistent with a mechanism in which an increasing fraction of the porphyrin triplets is intercepted with increasing BE concentration; no further increase in upconverted fluorescence intensity occurs when the TEET is complete. At still higher concentrations of the BE, self-quenching of the triplets might have been expected, but the self-absorption corrections were too large in this concentration range to determine accurate fluorescence intensities. In any case, the data are all entirely consistent with steps 2−6 in the mechanism of Baluschev et al.[4]

The ZnTPP−C343 pair does not admit efficient TEET because the triplet state of the potential coumarin acceptor lies at least 3000 cm^{-1} higher than that of the ZnTPP donor. Although TEET could occur via thermal activation, the fractional population of thermally activated porphyrin triplets, $[T_1{}^*]/[T_1]$, will be $<10^{-6}$ at room temperature when 3000 cm^{-1} of vibrational energy is required to bridge the electronic energy deficiency. Thus an activated TEET process is not competitive. This leaves only the TTA−SEET process of Baluschev et al.[4d,e] or some other mechanism to effect photon upconversion in this system. To our considerable surprise, relatively efficient photon upconversion was observed in the ZnTPP−C343 system, as shown in Figure 6. Note that the corrected emission spectra show that the S_2 emission is apparently "quenched" with a concomitant increase in the fluorescence intensity of the C343, yielding a sharp isoemissive point at ca. 21 850 cm^{-1}. This might lead one to conclude that the blue emission of the C343 arises from TTA in the porphyrin followed by SEET to the blue emitter via the Baluschev mechanism. However, the following considerations reveal that the photon upconversion process does not involve SEET but instead proceeds via a mechanism not previously proposed in these systems.

The ZnTPP steady-state S_2 fluorescence "quenching" data of Figure 6 can be cast in Stern−Volmer form as shown in Figure 7. This plot is linear over more than 2 orders of magnitude, and the slope yields a very large Stern−Volmer constant, $K_{SV} = k_Q\tau_D = 2.2(5) \times 10^5$ M^{-1}, where k_Q is the rate constant for the "quenching" process (which is assumed to be SEET for analysis purposes) and τ_D is the lifetime of the energy donor. We do not know the lifetime of the perturbed S_2 state of ZnTPP that is giving rise to the delayed emission by TTA, but the lifetime of a dilute ensemble of one-photon Soret-excited ZnTPP molecules in benzene is known precisely at 1.45 ps.[20] Assuming the SEET mechanism of Balushev et al.[4d,e] and using $\tau_D = 1.45$ ps yields a calculated value for $k_Q = 1.6 \times 10^{17}$ M^{-1} s^{-1}, which is at least 7 orders of magnitude larger than the diffusion-controlled limit for a bimolecular process in benzene at room temperature. Even allowing that the lifetime of the donor in the unrelaxed encounter complex may be substantially different from 1.45 ps and that SEET will occur efficiently over a much longer distance than the diffusion-controlled hard sphere one, these data prove that the energy donor cannot be the S_2 state of ZnTPP that is the product of the porphyrin triplet TTA process. That is, the SEET mechanism is not responsible for producing the photon-upconverted blue emission observed in the C343 acceptor.

This conclusion is confirmed by calculations of the rate of SEET in the ZnTPP−C343 system using Förster's theory of fluorescence resonant energy transfer (FRET).[38] For a point dipole system, the rate constant for energy transfer from an excited donor molecule (D*) to an acceptor molecule (A) is given by the equation

$$k_{D^*A} = \frac{1}{\tau_D}\left(\frac{R_0}{R}\right)^6 \tag{10}$$

where τ_D is the lifetime of the excited donor molecule in the absence of the acceptor, R is the distance between the donor and the acceptor molecules, and R_0 is the critical energy transfer (or Förster) distance at which the rate of energy transfer from the donor to acceptor has the same probability as the rate of spontaneous excited-state deactivation of the donor. R_0 is given by

$$R_0{}^6 = \frac{9000(\ln 10)\kappa^2\phi_D}{128\pi^5 n^4 N}\left(\frac{\int_0^\infty F_D(\bar{v})\varepsilon_A(\bar{v})\,d\bar{v}/(\bar{v})^4}{\int_0^\infty F_D(\bar{v})\,d\bar{v}}\right) \tag{11}$$

where ϕ_D is the fluorescence quantum yield of the donor, n is the refractive index of the medium, N is Avogadro's number, and the term in brackets is J, the integral of the spectral overlap between the normalized emission spectrum (F_D) and the acceptor absorption spectrum expressed in terms of the molar absorptivity (ε_A) as a function of wavenumber, $\bar{v}$. κ^2 is a factor that accounts for the distribution in the orientations of the transition dipole moments of the donor relative to those of the acceptor and takes on a value of 2/3 for a random orientation distribution in fluid solution.

The Förster FRET parameters for the SEET process of Baluschev et al.,[4d,e] step 8, were calculated for the ZnTPP(S_2)−C343(S_0) system using the PhotochemCAD program.[39] With $J = 1.65 \times 10^{-13}$ cm^6 from the measured spectra,

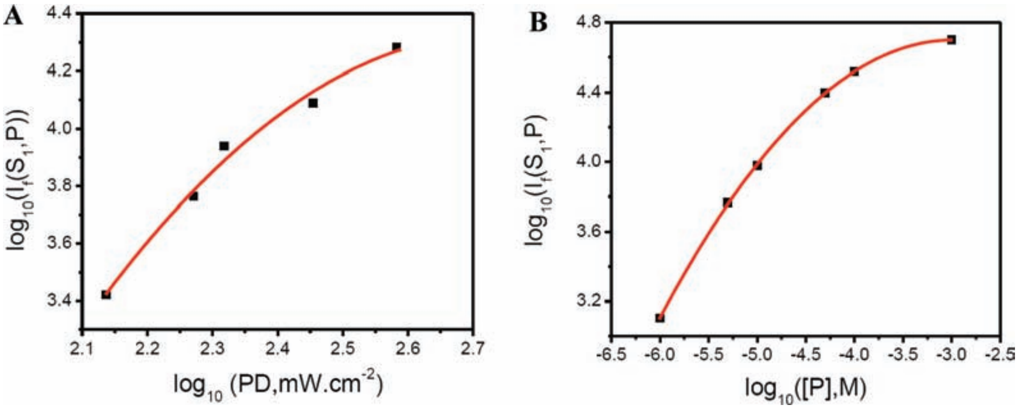


Figure 5. (A) Plot of the $\log_{10}$ of the S_1 fluorescence intensity of perylene, P, vs the $\log_{10}$ of the power density (PD) of the excitation laser for 532 nm (18 797 cm^{-1}) cw illumination of a 1.0×10^{-4} M ZnTPP solution in degassed benzene containing 1.0×10^{-4} M perylene. (B) Plot of $\log_{10}$ $I_f(S_1,P)$ (corrected intensities) vs $\log_{10}$ [P]. Experimental conditions are the same as in panel A except that different concentrations of perylene were employed at a fixed excitation power density of 0.28 W cm^{-2}.

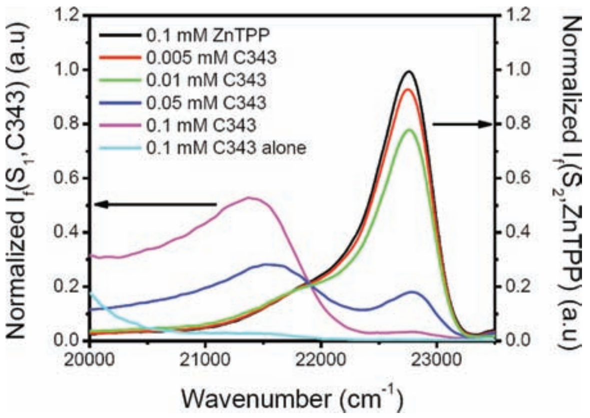


Figure 6. Upconverted fluorescence spectra obtained from 1.0×10^{-4} M ZnTPP with added C343 in degassed benzene. Samples were excited in rectangular geometry with a 0.28 W cm^{-2}, 532 nm (18 797 cm^{-1}) cw laser and a spectrometer with a 3.6 nm emission bandpass. The spectra were corrected for detector response and for reabsorption effects.

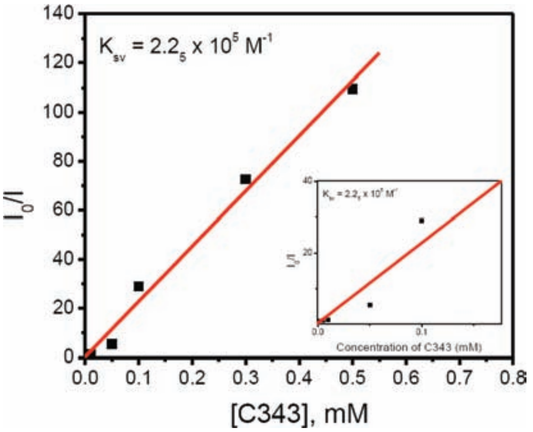


Figure 7. Stern−Volmer plot of I_0/I vs the millimolar concentration of C343 in a solution containing 1.0×10^{-4} M ZnTPP in degassed benzene. Samples were excited in rectangular geometry by a 532 nm (18 797 cm^{-1}) cw laser at a power density of 0.28 W cm^{-2} and a spectrometer with a 3.6 nm emission bandpass. The insert shows the lower portion of the graph in greater detail.

this calculation yields $R_0 = 17.4$ Å and $k_{D*A} = 1.25 \times 10^{10}$ s^{-1}. The latter is to be compared with the observed[20] unquenched ZnTPP(S_2) decay rate of $1/\tau_D = 6.9 \times 10^{11}$ s^{-1} and leads to a maximum energy transfer efficiency of less than 2% for the SEET mechanism. Because the platinum and palladium porphyrins used by Baluschev et al.[4] have S_2 lifetimes that are at least 2 orders of magnitude shorter than that of ZnTPP (see Supporting Information), BE emission intensities such as those reported cannot arise via a simple SEET mechanism.

We thus look for an alternate mechanism of photon upconversion in the ZnTPP−C343 system and, by extension, in other systems for which it is a model. The first possibility is that ZnTPP and C343 form a ground-state complex that absorbs a significant fraction of the excitation energy. However, there is no evidence in the absorption spectra of the ZnTPP−C343 mixtures of an additional band due to such a complex. Indeed the absorbance of 0.10 mM ZnTPP at 532 nm remains almost constant with the addition of up to 1.0 mM C343. We therefore dismiss this ground-state complex hypothesis and consider instead the possibility that aggregation of ZnTPP and C343 occurs while the ZnTPP is in its triplet state. Quantitative evidence supporting this hypothesis is obtained from the Stern−Volmer plot shown in Figure 7. The measured value of $K_{SV} = 2.2(5) \times 10^5$ M^{-1} and the value of the quenching rate constant at the diffusion limit may be used to obtain an upper limit for the lifetime of the energy donor, τ_D. With $k_Q \leq k_{diff} = 1.0 \times 10^{10}$ M^{-1} s^{-1}, the latter value appropriate for benzene solution at room temperature, then yields $\tau_D \geq 2.2 \times 10^{-5}$ s, which is typical of triplet species but rather shorter than the range of lifetimes measured for excited triplet ZnTPP (see Table 1). The intermediate cannot be the lowest triplet of C343 on energetic grounds, so we propose that the required species is a triplet exciplex[40,41] formed by the complexation of triplet ZnTPP with ground state C343. The new mechanism for photon upconversion then becomes steps 2 and 3, followed by

$$T_1(MP) + S_0(BE) \rightleftarrows {}^3(MP\cdots BE) \qquad (12)$$

$${}^3(MP\cdots BE) + T_1(MP) \rightarrow 2S_0(MP) + S_1(BE) \qquad (13)$$

where the blue emitter in this case is C343. The required quadratic dependence of the intensity of the S_1 emission from C343 on the incident power density is maintained in this system, as shown in Figure 8.

If the exciplex association and dissociation reactions in step 12 are fast compared with (i) heteromolecular TTA, process 13, which should be the case at low excitation powers, and (ii)

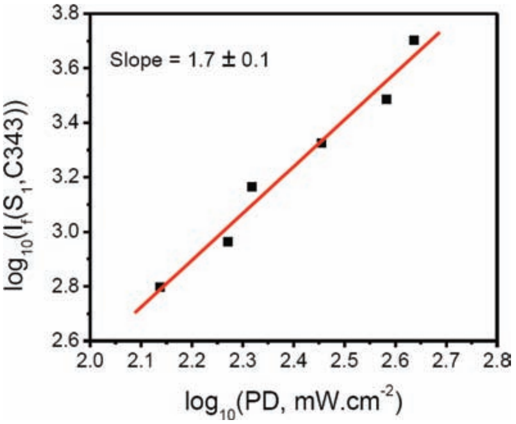


Figure 8. Plot of the $\log_{10}$ of the S_1 fluorescence intensity of C343 vs. $\log_{10}$ of the power density of the excitation laser for a degassed solution containing 1.0×10^{-4} M ZnTPP and a 5.0×10^{-5} M C343 in benzene. Samples were excited in front-face geometry with a 532 nm (18 797 cm^{-1}) cw laser, and the intensities were recorded with a fluorometer with a 3.6 nm emission bandpass.

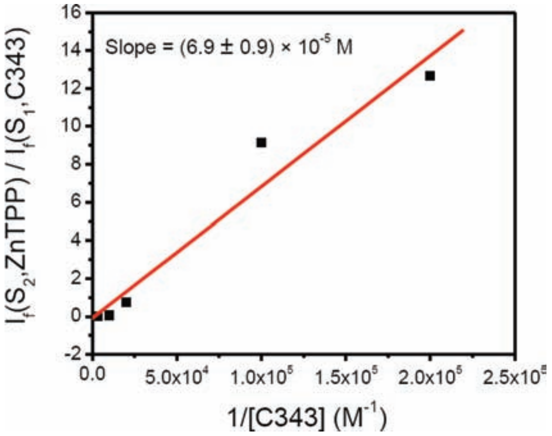


Figure 9. Plot of the ratio, R_f, described in eq 15 vs the inverse of the molar concentration of C343 in a 0.10 mM solution of ZnTPP in deoxygenated benzene at room temperature. The excitation conditions are the same as those described in Figure 6.

the rate of direct radiationless relaxation of the triplet exciplex, step 14 below, which should also be the case given the long lifetimes of such exciplexes (*vide infra*),

$$^{3}(\mathrm{MP}\cdots\mathrm{BE}) \rightarrow \mathrm{S}_0(\mathrm{MP}) + \mathrm{S}_0(\mathrm{BE}) \qquad (14)$$

then the ratio of the intensities of S_2 emission from the ZnTPP produced by TTA in the triplet prophyrin to S_1 emission in C343 produced by TTA of the triplet exciplex and the triplet porphyrin will be inversely proportional to the [BE]. The precise relationship is given by expression 15 and is derived in the Supporting Information:

$$R_f = \frac{I_{f,S2}}{I_{f,S1}} = \frac{\phi_{f,S_2}}{\phi_{f,BE}}\frac{k_7}{k_{13}}\frac{1}{K_{as}[\mathrm{BE}]} \qquad (15)$$

Here ϕ_{f,S_2} and $\phi_{f,BE}$ are the quantum yields of ZnTPP S_2 and C343 blue emitter S_1 fluorescence, respectively, k_7 and k_{13} are the rate constants for bimolecular TTA in the porphyrin and between the porphyrin and the triplet exciplex, respectively, and K_{as} is the equilibrium constant for associative formation and dissociation of the triplet exciplex. Figure 9 shows that the data exhibit the expected linear relationship between R_f and $[\mathrm{BE}]^{-1}$. A value of K_{as} can be obtained from the slope (6.9×10^{-5} M) and the quantum yields (see Table 1) if one can obtain values for the two rate constants for TTA. Assuming the latter are approximately equal gives $K_{as} = 24\ \mathrm{M}^{-1}$, a reasonable value if the triplet exciplex is only weakly bound.[40,41]

Direct spectroscopic evidence supporting the formation of such triplet exciplexes under TTA conditions will be difficult to obtain because the ZnTPP–C343 system absorbs throughout the visible region of the spectrum and because intense fluorescence is also observed in the blue–green and in the red–near-infrared (with excitation and scattered light centered at 532 nm). Nevertheless, strong evidence supporting the efficient formation of triplet metalloporphyrin exciplexes having lifetimes lying in the predicted range exists in the literature.[40,41] Whitten and coworkers[40] were the first to report the observation of such exciplexes, and their properties have been thoroughly investigated by Kapinus et al.[41] The following facts appear to be well-established: (i) In nonpolar solvents, the quenching of triplet porphyrins occurs via the formation of triplet exciplexes. (ii) The lifetimes of a wide range of porphyrin triplet exciplexes have been measured by transient absorption techniques. These lifetimes lie in the tens of microseconds to milliseconds range and depend on the nature of both the triplet metalloporphyrin and the quencher. (iii) The triplet exciplex lifetimes are mildly correlated with the extent of charge transfer in the complex; the longest-lived triplet exciplexes appear to be formed between good electron-donating metalloporphyrins and complexation partners that are weak electron acceptors. (iv) At low quencher concentrations, complexation results only in a reduction in the triplet porphyrin lifetime, but at higher quencher concentrations a longer-lived species grows in. The latter observations suggest that the lifetime of the initially formed triplet exciplex may be shorter than that of the triplet metalloporphyrin itself, that decay of the unperturbed triplet exciplex leads to triplet deactivation, and that further aggregation of a triplet exciplex with quencher results in a still longer lived triplet species.

The triplet lifetime of ZnTPP in fluid, deoxygenated, nonpolar solution is reported to lie in the 0.6–1.2 ms range,[34,35] so a triplet exciplex would be expected to have a lifetime that is significantly shorter than this. Thus the estimate (*vide supra*) of the lifetime of the triplet exciplex between ZnTPP and C343 is of the required order of magnitude. We conclude that an exciplex intermediate that participates in effective heteromolecular TTA leads to the observed blue emission in this model system. The idea that heteromolecular three-center TTA operates in these photon upconversion systems is novel. Nevertheless, such processes are well-established for excited singlet states in multichromophoric arrays, and the basic elements of the theory of energy pooling in three-center systems have been outlined by Jenkins and Andrews.[42]

Conclusions

Photon upconversion in degassed fluid solutions at room temperature has been studied here in two model porphyrin–BE systems. The first, exemplified by ZnTPP–perylene, is one in which the triplet of the porphyrin lies at a higher energy than that of the quencher. In this system, TEET occurs with high efficiency and upconversion is effected by TTA in the quencher triplet state. The second system, explored via experiments with ZnTPP–C343, is one in which the triplet energy of the porphyrin absorber lies at an energy substantially lower than that of the BE, forcing a different energy-transfer mechanism.

We demonstrate that the preferred upconversion mechanism involves the formation of a triplet exciplex between the porphyrin triplet and the ultimate blue emitter, followed by heteromolecular annihilation of the triplet exciplex with a second porphyrin triplet in a three-center process.

Irrespective of the detailed mechanism of photon upconversion in cases where the triplet energy of the BE lies higher than that of the metalloporphyrin, it is clear that the mechanism of SEET proposed by Baluschev et al.[4d,e] cannot hold either in the ZnTPP−BE system examined here or in the PdOEP−BE and PtOEP−BE systems studied by them. Those metalloporphyrins that have short-lived S_1 states, large intersystem crossing yields, and long-lived lowest triplet states and may be tailored to absorb strongly in the near infared regions of the spectrum are also nonfluorescent from the upper excited singlet states accessed on one-photon excitation in their Soret bands. A simple calculation based on a Strickler−Berg[43] estimate of the Soret radiative rate constant ($k_r \approx 5 \times 10^8$ s^{-1}) and a measurement of the upper limit for the fluorescence quantum yield (in the absence of measurable Soret band emission, $\phi_f < 10^{-5}$, see Supporting Information) leads one to the conclusion that the lifetimes of the upper excited singlet states of those heavy-metal containing porphyrins commonly used as sensitizers in photon upconversion schemes lie in the tens of femtoseconds region. This is about 2 orders of magnitude shorter than the 1.45 ps S_2 lifetime[20] of ZnTPP used in the model system studied here. Without prior aggregation of the BE with the porphyrin, efficient energy transfer to the BE by a SEET mechanism is therefore impossible. In the solid state and in polymer films, aggregation of the metalloporphyrin with itself and with the BE might still allow upper-state SEET to occur in favorable systems. However, even in these cases the annihilation of triplet excitons,[44] whose properties are determined in large measure by the state of aggregation of the system, is likely to dominate the excited-state annihilation mechanism and thus the overall mechanism of photon upconversion.

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Supporting Information Available: Absorption spectra, TTA fluorescence spectra showing effects of titrating pyridine into benzene solution of ZnTPP, method of estimating the S_2−S_0 fluorescence quantum yield and S_2 lifetime of PdOEP in solution, derivation of eq 15, and fluorescence reabsorption correction procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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