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Porphyrin–Anthracene Complexes: Potential in Triplet–Triplet Annihilation Upconversion

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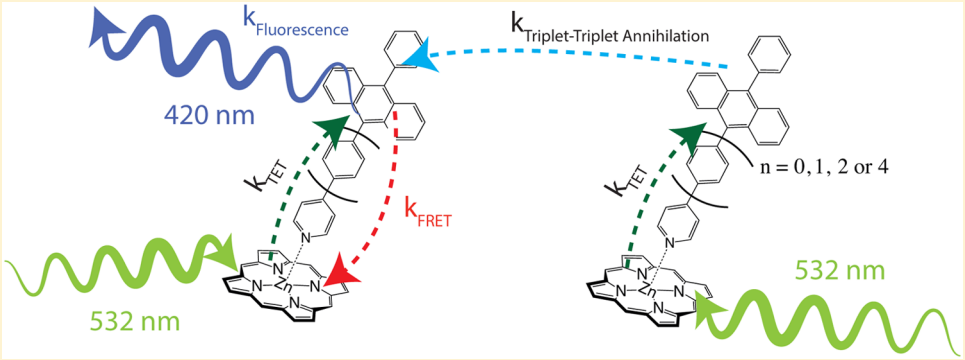
Supporting Information



ABSTRACT: Triplet–triplet annihilation photon upconversion (TTA-UC) systems contain both an absorbing and an emitting molecule, the sensitizer and annihilator, respectively. Through a series of energy-transfer steps, two low frequency photons can be combined into one high frequency photon. In organic solvents, the required energy transfer steps are limited by diffusion and are relatively efficient. In solid-state systems, however, the diffusion is slower, which usually results in lower efficiencies for these systems. An interesting way around this is to connect the sensitizer and annihilator. In order to increase understanding of the TTA-UC process in supramolecular systems, we synthesized four pyridine-substituted anthracene annihilators capable of coordinating axially to a zinc octaethylporphyrin sensitizer with a maximum binding constant of 6000 M^{-1} in toluene. This is a first example of a sensitizer–annihilator coordination complex for TTA-UC. Both the upconversion efficiency and the parasitic quenching of excited annihilator singlets by the sensitizer through Förster resonant energy transfer (FRET) were studied. On the basis of the findings herein, possible strategies for future supramolecular TTA systems with minimized FRET quenching are discussed.

INTRODUCTION

Energy transfer in porphyrin–chromophore assemblies have been long studied. The interest stems from nature's way, in photosynthesis, of using antenna structures to funnel absorbed photon energy to a reaction site. This concept has been employed in many photochemical systems,[1,2] and it is perhaps surprising that little attention has been focused on utilizing this for sensitized triplet–triplet annihilation (TTA) photon upconversion.

The process of generating high energy photons from two low energy photons is commonly known as photon upconversion (UC). Photon upconversion through TTA of organic chromophores, which can generate upconverted emission from incoherent low intensity light,[3−9] has been suggested[10−13] and, to some extent, demonstrated to be a viable means of utilizing sub-band-gap photons in solar energy applications.[14−21]

Typically, triplet–triplet annihilation upconversion occurs in a bimolecular system containing a triplet sensitizer, commonly palladium or platinum porphyrins, and an annihilator species, typically polyaromatic molecules. The process is described in Figure 1. First, a low energy photon is absorbed by the sensitizer (S), which readily undergoes intersystem crossing (ISC) to form its first excited triplet state (^{3}S*). Subsequently, the triplet state of the annihilator (^{3}A*) is populated through a triplet-energy transfer (TET) process from the sensitizer. Two triplet excited annihilators then interact and undergo TTA, and this might result in the formation of one singlet excited annihilator (^{1}A*) and one annihilator in the ground state (^{1}A). The singlet excited annihilator subsequently relaxes to the ground state through fluorescence, emitting a photon of higher frequency than the ones initially absorbed.

In solution, with suitable concentrations, the energy-transfer steps required for TTA-UC are efficient. For example, the

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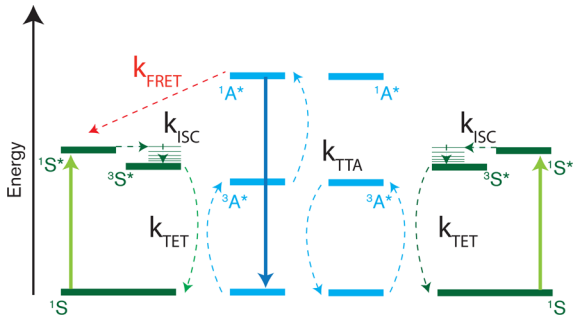

Figure 1. Jablonski diagram explaining the triplet−triplet annihilation upconversion process. A sensitizer first absorbs a low energy photon and rapidly populates its first triplet excited state after ISC from the singlet state. The triplet energy is then transferred to an annihilator species through TET, generating one triplet excited annihilator molecule. When two triplet excited annihilator molecules come together they can undergo TTA to form a singlet excited annihilator which can deactivate to its ground state by emitting a photon. If the sensitizer and annihilator are in close proximity, e.g., when connected, a new deactivation pathway is possible, namely singlet energy transfer of the excited singlet annihilator, short-circuiting the system.

triplet energy transfer from sensitizer to annihilator can be almost quantitative with a large excess of the annihilator. For applications, solid-state TTA-UC systems are required, and the general direction of the field is, thus, toward such systems. However, in solid-state materials the energy-transfer steps are not as straightforward to control, and therefore, it is important to study sensitizer−annihilator assemblies.[22] For example, Kimizuka and co-workers have recently presented an elegant way of enhancing the triplet-migration and subsequent TTA in metal−organic framworks (MOFs) leading to near-unit TTA efficiency.[23,24] However, the TET from sensitizer to the annihilator in these studies was not as efficient as in solution-dissolved systems, and further optimization of this energy-transfer step was suggested.[23,24]

As TTA-UC requires energy transfer from a sensitizer to an annihilator, the idea of connecting the two to enhance the energy transfer in solid systems is not completely new, and examples of covalently linked sensitizer−annihilator dyads in solution exist in the literature.[25−28] However, these systems were less efficient than the corresponding nonconnected system due to quenching of the upconverted singlet excited state through energy transfer back to the sensitizer. Understanding the effect on TTA-UC in supramolecular sensitizer−annihilator assemblies is necessary for future applications that would require efficient, solid-state upconversion materials.

We have chosen to investigate a series of sensitizer−annihilator complexes, their upconversion properties, and the parasitic singlet energy transfer from annihilator back to the sensitizer. It has been suggested previously that axial coordination of anthracene to a Sn(IV) porphyrin excludes singlet energy transfer through Förster resonance energy transfer (FRET) from the anthracene to porphyrin.[29] We therefore designed, synthesized, and studied four anthracene derivatives capable of axially coordinating to a zinc porphyrin and here present a first example of sensitizer−annihilator coordination complexes used for TTA-UC. The possible energy-transfer steps in the coordinated systems are schematically illustrated in Figure 1.

The annihilator species in the study are based on 9,10-diphenylanthracene (DPA), which is one of the benchmark annihilators.[21] Pyridine as a terminal group on one side of the phenylanthracene was chosen in order to achieve coordination of the nitrogen lone pairs to the zinc(II) octaethylporphyrin (ZnOEP) metal center. The terminal pyridine was separated from the anthracene moiety with 0, 1, 2, or 4 phenyl groups, Ph_{1-5}AnPyr in Figure 2. For solubility reasons, Ph_5AnPyr was modified with solubilizing 2-ethylhexyl side chains.

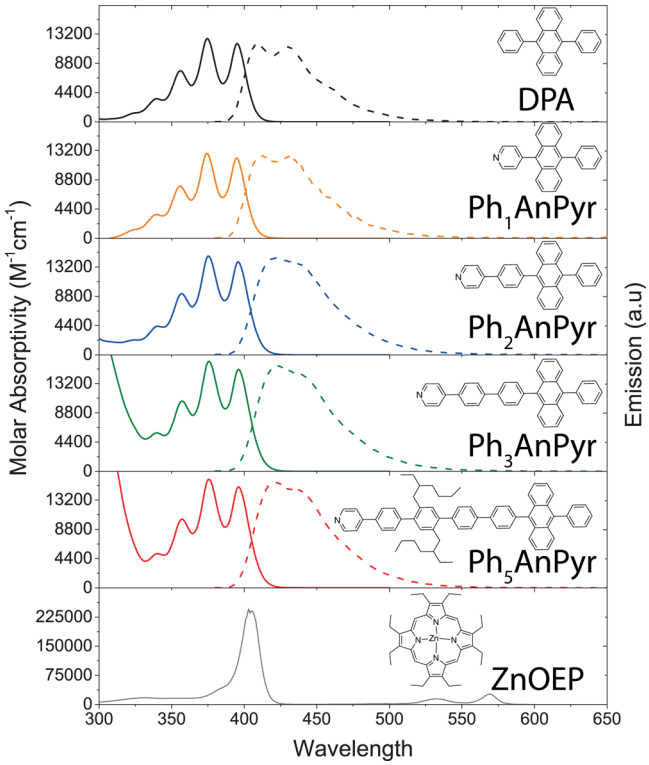

Figure 2. Molar absorptivity (solid) and normalized fluorescence (dashed) of the studied annihilators DPA (black), Ph_1AnPyr (orange), Ph_2AnPyr (blue), Ph_3AnPyr (green), and Ph_5AnPyr (red) and the sensitizer ZnOEP (gray).

As sensitizer, a metal porphyrin with a transition metal capable of bonding with the nitrogen lone pairs had to be used, and therefore, the standard palladium and platinum octaethylporphyrins commonly used with DPA could not be utilized. However, as zinc porphyrins also have relatively high triplet yields, 90%,[2,30] the similar zinc(II) octaethylporphyrin (ZnOEP) was used. We show that upconverted emission is obtained for both coordinated and noncoordinated annihilators with ZnOEP, and we also study the unwanted singlet energy transfer from anthracene back to ZnOEP. Based on the results presented here, we also discuss the limiting factors in the present coordinating annihilator−sensitizer system and, thus, highlight design criteria for future annihilator−sensitizer coordination systems.

EXPERIMENTAL METHODS

The synthetic route and detailed procedures to the new molecules Ph_{2-5}AnPyr are described in the Supporting Information (Figure S1), including ^1H and ^{13}C NMR spectra (Figures S2−S19). Absorption spectra were recorded on a Cary 4000 spectrophotometer. The binding constants of the anthracene derivatives to ZnOEP were determined from the changes in the absorption spectra during the titration of the

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annihilators by performing a single value decomposition (SVD) analysis[31] in MATLAB; for details, see the Supporting Information (Figures S20−S24).

Fluorescence quantum yields were determined in dilute[32] and degassed samples relative to DPA (Φ_f = 1.0 in degassed toluene)[33] in 1 cm quarts cuvettes. A Spex Fluorolog τ3 spectrofluorimeter (JY Horiba) was used to record steady-state emission spectra. Fluorescence lifetimes were determined on a time-correlated single-photon counting (TCSPC) setup using a PicoQuant pulsed laser diode (377 nm) and a PMT detector (10000 peak counts in the top channel, 4096 channels) with an instrument response function fwhm of 64 ps.

Nanosecond transient absorptions measurements were performed on a home-built system with a Surelite Continuum Nd:YAG laser equipped with an OPO generating a 7 ns (fwhm), 537 nm pump beam. A quartz−halogen lamp equipped with a monochromator was used as the probe light, and a monochromator together with a five-stage PMT coupled to an oscilloscope was used for recording the transient. All photophysical measurements were carried out in analytical-grade toluene (99.99%) from Sigma-Aldrich as lower grade toluene resulted in a shift in the ZnOEP absorption similar to that of coordinated ZnOEP. Degassed samples used in the upconversion intensity study and transient absorption measurement were permanently sealed in Pyrex test tubes (d = 1 cm) after degassing following a freeze−pump−thaw procedure described in the Supporting Information.

Upconversion emission was recorded on above-mentioned Spex Fluorolog using a 532 nm green laser-pointer (I_{max} = 33.8 mW, A = 0.057 cm^2) as the light source and a graduated neutral density filter to vary the intensity. For the viscous upconversion samples containing polystyrene a 532 nm green laser-pointer (I_{max} = 80 mW, A = 0.027 cm^2) was used. The upconversion quantum yield (Φ_{UC}) was determined by relative actionometry using Cresyl Violet in methanol (Φ_r = 0.54)[34] as the reference in accordance to eq 1

$$\Phi_{UC} = \Phi_r \frac{A_r}{A_x}\frac{F_x}{F_r}\frac{I_r}{I_x}\frac{\eta_x^2}{\eta_r^2} \quad (1)$$

where A_i is the absorption at the excitation wavelength, F_i is the integrated corrected emission spectra in wavenumbers, I_i is the excitation intensity, and η_i is the refractive index of the solvent; subscripts x and r denote the sample and reference, respectively. The reference was measured at the highest excitation intensity in each measurements series. It is important to note that the maximum upconversion quantum yield is 50% as two low energy photons are consumed to produce one photon of higher energy.

RESULTS

As observed previously, extending the DPA moiety in the para-position of one of the phenyl groups only alters the absorption and fluorescence characteristics to a minor extent.[35] As seen in Figure 2, the molar absorptivity increases with more phenyl groups and a new transition at higher energies than the characteristic DPA absorption is observed for the compounds with extended phenyl groups. The fluorescence quantum yield (Φ_f) in toluene is high for all derivatives (Table 1), although the derivatives with extended phenyl groups have slightly lower Φ_f, around 0.85.

Coordination to ZnOEP was confirmed by following the shift of the ZnOEP absorption toward the red while titrating the pyridine containing derivatives, Figures S21−S24. The observed shifts were similar to that of ZnOEP with pyridine. The titration data and fitting procedure is described in the Supporting Information. K_B is around 6000 M^{-1} for the bridged compounds Ph_2AnPyr, Ph_3AnPyr, and Ph_5AnPyr. Ph_1AnPyr with the pyridine group directly on the anthracene unit has a lower binding constant of 2300 M^{-1} and as expected DPA showed no coordination to ZnOEP. Coordination was also confirmed by H^1 NMR spectroscopy where the anisotropic effect of the porphyrin ring-current drastically shifts the pyridine proton signals upfield (Figures S16−S19).

Table 1. Photophysical Properties of Coordinating Annihilators in Degassed Toluene Solutions

compd	Φ_f	τ_f (ns)	K_B (M^{-1})
DPA	1.0[33]	6.97[35]	0
Ph_1AnPyr	0.96 ± 0.020[35]	5.29 ± 0.01	2300
Ph_2AnPyr	0.85 ± 0.019	3.55 ± 0.01	5900
Ph_3AnPyr	0.85 ± 0.003	3.17 ± 0.01	5800
Ph_5AnPyr	0.86 ± 0.052	3.33 ± 0.01	6000

The sensitizer−annihilator complex lifetime could be estimated from the binding constants. Assuming a diffusion limited association constant (10^9 M^{-1} s^{-1}), a lifetime of ∼6 μs was estimated for a binding constant of 6000 M^{-1} (see the Supporting Information for details). Even for a smaller assumed association constant of 10^8 M^{-1} s^{-1}, the lifetime, ∼60 μs, is shorter than the unperturbed excited triplet state lifetimes of ZnOEP (200 μs, see Supporting Information) and anthracene derivatives.[35] With a short complex lifetime of 6−60 μs, it is likely that triplet−triplet annihilation and subsequent upconverted emission do not occur from a bound anthracene derivative. This could be beneficial as the parasitic singlet energy transfer from the upconverted anthracene singlet through FRET is distance dependent and a dissociated anthracene is, therefore, less likely to be quenched by the sensitizer.

To study the UC efficiency of the coordinating annihilators, samples were prepared with a relatively high annihilator concentration (2.5 mM) and low sensitizer concentration (1 μM) resulting in ∼90% of the sensitizer bound to an annihilator. For solubility reasons, Ph_3AnPyr could only be prepared in 0.23 mM with 1 μM ZnOEP (corresponding to 67% bound sensitizer). Efficient upconverted emission, Φ_{UC}, from 3 to 20% (Figure 3), was observed from both coordinated and noncoordinated annihilators despite the increased chance of quenching of the annihilator singlet through FRET when connecting the sensitizer and annihilator.[25−28] There can be multiple explanations for why the coordinated systems show only minor upconversion quenching through FRET, one being the weak complexation and short complex lifetime allowing the TTA step to occur between unbound (dissociated) species. Figure 3 shows the upconversion emission intensity and upconversion quantum yield (ϕ_{UC}) dependence on excitation power density.

A decrease in the emission was observed for Ph_1AnPyr compared to DPA even though they previously have been shown to perform similarly in noncoordinating systems.[35] The reason for this can be that a small fraction of the TTA events still occur for complexed annihilators, followed by efficient singlet state quenching.

Annihilators with longer bridges (Ph_{2-5}AnPyr) display lower UC-emission intensity, even after considering the slightly lower

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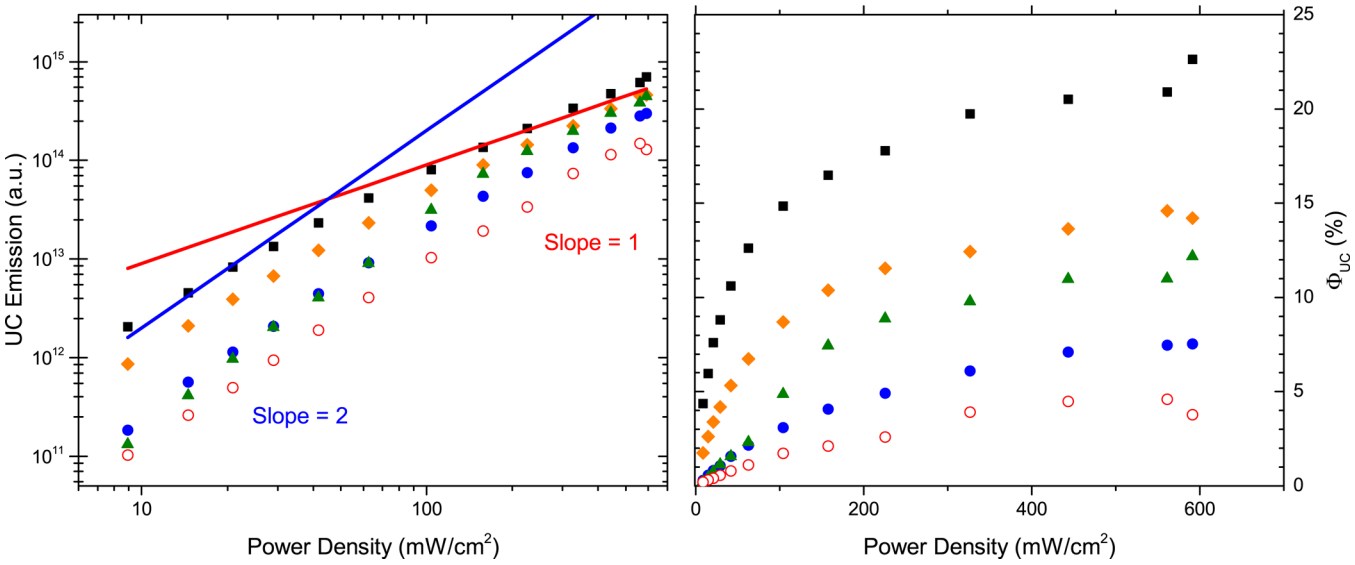

Figure 3. (Left) Upconverted emission plotted against excitation power (532 nm). (Right) Upconversion quantum yield. Samples of 1 μM ZnOEP sensitizer and 2.5 mM DPA (black squares), 2.5 mM Ph_1AnPyr (orange diamonds), 2.5 mM Ph_2AnPyr (blue circles), 0.23 mM Ph_3AnPyr (green triangles), and 2.5 mM Ph_5AnPyr (red open circles).

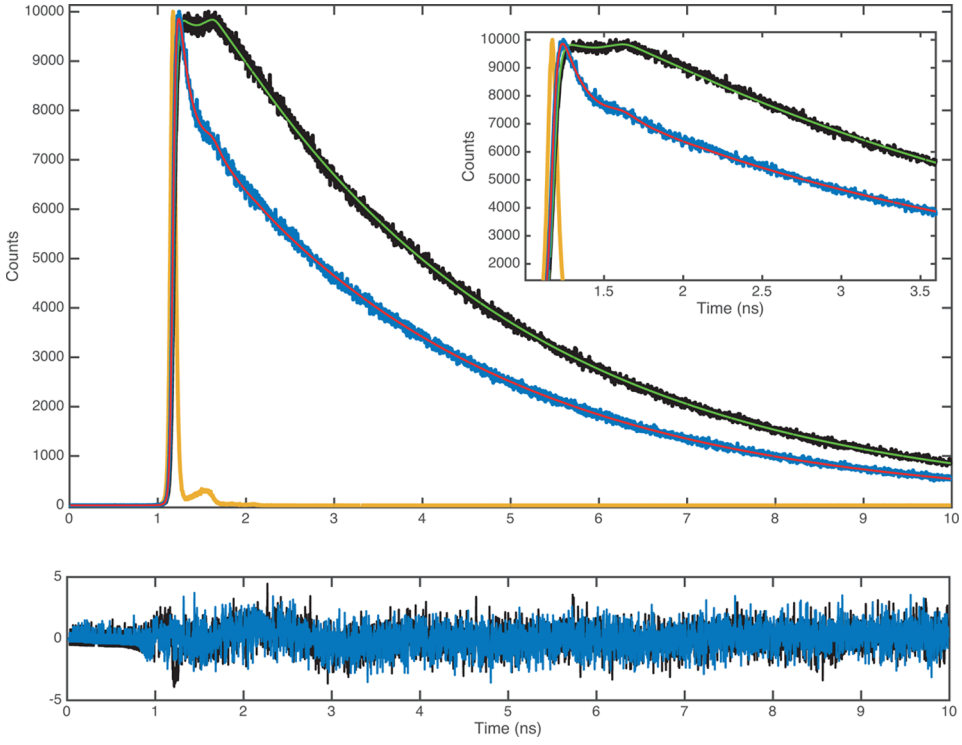

Figure 4. Upper: Fluorescence decay for Ph_5AnPyr (14 μM), alone (black) corresponding fit (green), with ZnOEP (140 μM) (blue), corresponding fit (red) and instrument response function (yellow). The bump at 2 ns for Ph_5AnPyr alone (black), is due to the instrument response. Lower: Residual to the fitted decays,Ph_5AnPyr, alone (black) and with ZnOEP (blue).

Φ_f. As TET occurs at least equally as fast as for the unbound annihilator DPA, and the longer bridges would reduce the FRET quenching compared to the shorter Ph_1AnPyr annihilator (vide infra), this decrease must originate from a less efficient TTA step, indicating that not every molecular collision between two triplet annihilators results in a TTA event yielding an excited singlet. This is also supported by the fact that the annihilators Ph_{2-5}AnPyr reach the linear upconversion regime[36] at higher excitation intensities compared to DPA and Ph_1AnPyr. Also, as for Ph_1AnPyr, some TTA events could occur by annihilators complexed to ZnOEP, which then would lead to quenching of the singlet excited state of the annihilator prior to emission, thus leading to a lower UC emission compared to DPA.

In an attempt to decrease the diffusion-controlled energy transfer, samples with a more viscous sample environment and low annihilator concentration were prepared. Annihilator (0.1 mM) and sensitizer (0.1 mM) were dissolved in toluene together with polystyrene (255 mg/mL, M_w = 160000 Da). However, at these low concentrations less than 5% of the

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sensitizer is complexed to an annihilator, assuming that the complex formation is unaffected by the addition of polystyrene. In these samples, DPA and Ph_1AnPyr display similar upconversion characteristics (Figure S25). The difference between the longer bridged annihilators is also smaller compared to the more concentrated low viscosity solutions (Figure S25).

Singlet Energy Transfer. To further understand the possible energy-transfer steps in the coordinating systems, the energy-transfer efficiency from a singlet excited anthracene derivative to a nearby ZnOEP was studied. This singlet energy transfer is expected to occur through FRET, where the anthracene moiety is the donor chromophore and ZnOEP the acceptor. Thus, the energy transfer from annihilator to sensitizer can be controlled by altering the donor−acceptor distance, the relative orientation, and the spectral overlap. Our choice of an axial anthracene ligand to the ZnOEP stemmed from the close to 90° angle expected between the acceptor and donor transition dipole moments. With a binding angle of 90°, singlet energy transfer through FRET would be prevented. In addition, the distance separating the donor and acceptor plays an important role, and both of these aspects were studied closer through careful analysis of the fluorescence quenching of directly excited anthracene in the presence and absence of the porphyrin acceptor.

The fluorescence decays were recorded for the anthracene derivatives (~15 μM) alone and for the mixture of anthracene derivative (~15 μM) and ZnOEP (0.14 mM). From these concentrations and the binding constants, the amount of complexed anthracene was calculated to ~40% of the total annihilator concentration. In Figure 4, the fluorescence decays of Ph_5AnPyr and Ph_5AnPyr−ZnOEP are shown. As seen in Figure 4, Ph_5AnPyr−ZnOEP shows a biexponential decay displaying two components, one being similar to the unbound Ph_5AnPyr and an initial fast decay of 152 ps. The proportion of this fast decay to the overall decay is ~40% suggesting that FRET occurs for all coordinated Ph_5AnPyr molecules. This corresponds to a transfer efficiency of 96% for the complexed annihilators. Similarly, a fast decay of 27 ps for the Ph_3AnPyr−ZnOEP complex was observed, and the faster fraction here corresponded to ~30% of the total decay, Figure S26. For the shorter bridged systems Ph_2AnPyr and Ph_1AnPyr higher time resolution was required, and the lifetimes for these complexes were not determined.

The efficiency of energy transfer through FRET (η_{FRET}) can be calculated from the lifetime of the donor−acceptor complex (τ_{DA}) and the donor alone (τ_D) according to eq 2.[37]

$$\eta_{FRET} = 1 - \frac{\tau_{DA}}{\tau_D} \tag{2}$$

The FRET energy transfer efficiency can also be determined from eq 3

$$\eta_{FRET} = \frac{R_0^6}{R_0^6 + r^6} \tag{3}$$

where r is the actual distance between donor−acceptor transition dipole moments and R_0 (in Å) is the characteristic distance corresponding to 50% energy transfer. R_0 is calculated from spectroscopic properties of the donor and acceptor by eq 4:

$$R_0 = 0.211(\kappa^2 n^{-4} \Phi_D \int_0^\infty F_D(\lambda)\epsilon_A(\lambda)\lambda^4 \, d\lambda)^{1/6} \tag{4}$$

In eq 4, κ^2 is an orientation factor (vide infra), n is the refractive index, Φ_D is the fluorescence quantum yield of the donor, F_D is the area normalized fluorescence of the donor, ϵ_A is the molar absorptivity (M^{-1} cm^{-1}) of the acceptor, and λ is the wavelength (nm). The integral is called the spectral overlap integral and is often denoted J.[37]

The distance r in eq 3 was determined from the Zn atom to the center of the anthracene core from AM1-optimized geometries of the complexes (Figures S27−S30). From the singlet lifetime quenching data and combining eqs 2 and 3 we determined R_0, Table 2, for Ph_3AnPyr and Ph_5AnPyr. This in turn allows for the experimental determination of the orientation factor, κ^2, from eq 4, Table 2.

Table 2. Fluorescence Lifetimes (τ_{DA}), FRET Efficiency (η_{FRET}), Inter-chromophore Distance (r), Förster Distance R_0, Orientation Factor (κ^2), and Binding Angle for Coordinated Annihilators

compd	τ_{DA} (ps)	η_{FRET} (%)	r[a] Å	R_0 (Å)	$\langle\kappa^2\rangle$	binding angle[b] (deg)
Ph_1AnPyr	<20	>99.6	8.0			
Ph_2AnPyr	<20	>99.4	12.2			
Ph_3AnPyr	27 ± 7	99.2 ± 0.2	17.3	38	0.19	75
Ph_5AnPyr	152 ± 10	95.4 ± 0.3	25.0	42	0.29	71

[a]Distance from Zn atom to center of anthracene core estimated from the AM1-optimized geometry of the complex. [b]Angle β in Figure 5.

Theoretically, κ^2, lies between 0 and 4 and is related to the angles between the donor and acceptor transition dipole moments as in eq 5. The angle α is the angle between the transition dipole moment of the donor and the vector connecting the transition dipole moments of the donor and acceptor; the connecting vector is here defined as the x-axis in Figure 5. The angle β is the corresponding angle for the acceptor. γ is the angle between the acceptor and donor transition dipole moments when projected in the same plane. These angles are illustrated in Figure 5a.[37,38]

$$\kappa^2 = (\cos\gamma - 3\cos\alpha\cos\beta)^2 \tag{5}$$

As the orientation factor is dependent on the angles between the donor and acceptor chromophores, apparent binding angles between Ph_{3-5}AnPyr and ZnOEP can be estimated from κ^2, Table 2. At room temperature, the dynamic complexation results in a distribution of angles, and the apparent binding angle can be viewed as a measure on how broad this distribution is. The more the apparent angle deviates from 90° the wider the distribution.

In 9,10-substituted anthracene, the transition dipole moment for the lowest electronic transition is located along the 9,10-carbons, but for a porphyrin the transition dipole moment for the lowest singlet transition is degenerate and oriented within the molecular plane (Figure 5). To calculate κ^2 for a degenerate case where there is 4-fold symmetry one can represent the degenerate transition dipole moments as two perpendicular transition dipole moments and calculate the average $\langle\kappa^2\rangle$ according to eq 6[38]

$$\langle\kappa^2\rangle = \frac{(\kappa_1^2 + \kappa_\perp^2)}{2} \tag{6}$$

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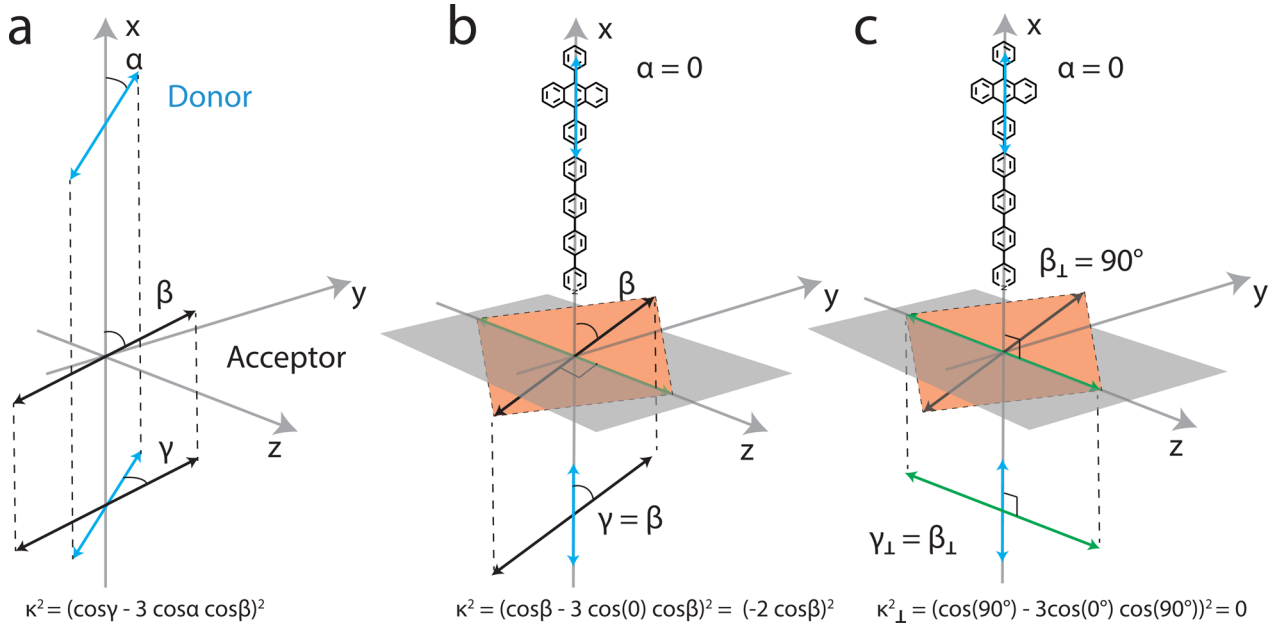

Figure 5. (a) Angles between donor (blue) and acceptor (black) transition dipole moments used for calculating the orientation factor, κ^2, for a donor−acceptor pair. (b) Transition dipole moment in anthracene derivatives (blue) and the degenerate transition dipole moments in ZnOEP are represented by two perpendicular transitions (green and black) spanning the porphyrin plane (orange). The *y*,*z*-plane is colored gray for clarity. Also illustrated are the angles relevant for the black transition dipole moment component in ZnOEP, β and γ. (c) As in b, now illustrating the angles relevant for the perpendicular dipole moment component (green arrow), $\beta_\perp$ and $\gamma_\perp$.

were κ_1^2 is the orientation factor calculated for an arbitrarily chosen transition dipole moment in the ZnOEP plane and $\kappa_\perp^2$ is the orientation factor calculated for the perpendicular transition dipole moment. As can be seen in Figure 5b,c, when two perpendicular transition moment components are chosen to represent the degenerate transition one of them could be selected to lie perpendicular to the anthracene transition moment and then the other component will be defining the projection of the porphyrin plane on the anthracene transition moment (angle β).

Parts b and c of Figure 5 show the two perpendicular transition dipole moment components used here. Combining eqs 5 and 6 with the angles defined in Figure 5b,c and averaging over all azimuthal angles (i.e., rotating the porphyrin plane around the anthracene long-axis), one obtains eq 7

$$\langle \kappa^2 \rangle = \frac{(-2\cos\beta)^2 + 0}{2} = 2\cos^2\beta \tag{7}$$

where β also corresponds to the apparent binding angle between the porphyrin plane and the annihilator transition moment. The calculated angles are 75° and 71° for Ph_3AnPyr and Ph_5AnPyr, respectively, Table 2. For a hypothetical binding angle of 90° no energy transfer through FRET would be observed.

DISCUSSION

First, it is interesting to examine why no notable increase in upconversion efficiency was detected in the coordinating samples. As will be discussed, this does not rule out the usefulness of coordinating the annihilator to the sensitizer in better optimized, systems. The upconversion quantum yield, Φ_{UC} is given by the product of the quantum yield of the triplet energy transfer (Φ_{TET}), the triplet−triplet annihilation quantum yield of forming an excited singlet annihilator (Φ_{TTA}), the intersystem crossing yield of the sensitizer (Φ_{ISC}), and the fluorescence quantum yield of the annihilator (Φ_f) as in eq 8:

$$\Phi_{UC} = \Phi_{ISC}\Phi_{TET}\Phi_{TTA}\Phi_f \tag{8}$$

Since Φ_{ISC} is a property of the sensitizer, we assumed it to be the same in both the coordinated and the noncoordinated system. Therefore, the difference in efficiency must be explained by either a decrease in Φ_f, through singlet quenching of the annihilator, by a decrease in Φ_{TTA} or by a less efficient triplet energy transfer step, (smaller Φ_{TET}).

Considering that the UC efficiency decreases more the longer the bridge becomes, which is opposite to the trend for Φ_f, and that there is a large excess of free annihilator in the samples, we conclude that the quenching of the singlet annihilator is not the main bottleneck in the present systems. We have previously shown that DPA and Ph_1AnPyr have very similar UC properties when a noncoordinating sensitizer is used,[35] suggesting that a lower Φ_{TTA} is not the explanation to the difference between these two annihilators in the current system. This leaves the triplet energy transfer as the limiting step.

We determined the rate constant for triplet energy transfer through diffusion in toluene to 7.8×10^8 M^{-1} s^{-1} (Figure S31) from nanosecond transient absorption measurements of ZnOEP and DPA, the corresponding rate constant for platinum porphyrin is in the range of 2×10^9 M^{-1} s^{-1}. This can be understood by the difference in triplet state energy of the sensitizer, which is lower for ZnOEP leading to a smaller driving force for TET. The triplet energy of ZnOEP is about 1.78 eV,[39] and we estimated the triplet energy for DPA and Ph_1AnPyr to 1.72 and 1.73 eV, respectively.[35] Since the singlet energy of ZnOEP is lowered upon coordination to the annihilators (vide supra) it is also likely that the triplet energy level is affected, leading to a yet smaller driving force and, thus, less efficient TET. This can, of course, be circumvented in

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future systems using sensitizer and annihilator pairs with better matched triplet energies.

Therefore, it is interesting to consider the case when TET is efficient, in such coordinating systems there are two possible ways of triplet energy transfer; either through the usual collisional transfer pathway or energy transfer through the bridge of the coordinating annihilator. In order to observe a difference in UC properties for the coordinating samples the triplet energy transfer must increase Φ_{TET} due to coordination. The energy-transfer efficiency from sensitizer to annihilator can be calculated from the fraction between the sensitizer triplet lifetime in presence and absence of annihilator (eq 9)

$$\Phi_{TET} = 1 - \frac{\tau}{\tau_0} \tag{9}$$

where τ_0 is the lifetime of the sensitizer alone and τ is the lifetime of the sensitizer in the presence of the annihilator. From the Stern–Volmer equation, the ratio of the lifetime quenching can be calculated for various annihilator concentrations

$$\frac{\tau_0}{\tau} = 1 + k_{TET}\tau_0[A] \tag{10}$$

where k_{TET} is the rate constant for triplet energy transfer and $[A]$ is the annihilator concentration. If we assume that in a coordinated sensitizer–annihilator pair the triplet energy transfer is faster than the triplet excited complex dissociation and therefore quantitative we can compare the fraction of coordinated ground-state sensitizers to the diffusional triplet energy transfer efficiency, Φ_{TET}, for various annihilator concentrations, and this is shown in Figure 6.

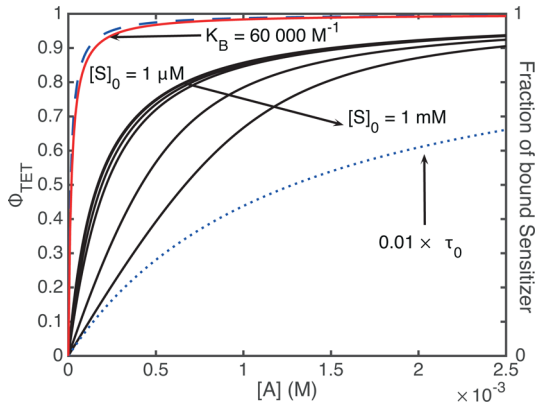

Figure 6. Calculated triplet energy transfer efficiency for diffusion-controlled energy transfer with a sensitizer lifetime of 200 μs (blue dashed) and 2 μs (blue dotted). The fraction of bound sensitizer calculated for K_B = 6000 M^{-1} and sensitizer concentrations between 1 μM and 1 mM (black) as well as the fraction of bound sensitizer calculated for K_B = 60000 M^{-1} and a sensitizer concentration of 1 μM (red).

In our present study, the maximum obtained binding constant is 6000 M^{-1}, and in Figure 6 the fraction of bound sensitizer is shown for various sensitizer–annihilator concentrations. Compared to the diffusive energy-transfer efficiency the fraction of bound sensitizer is constantly lower. This means that, even in the case with quantitative TET in a coordination complex, no increase in Φ_{UC} will be observed. There are two interesting conclusions from Figure 6. First, if the binding strength (K_B) can be increased by a factor of 10, the static energy transfer in complexed sensitizer-annihilator pairs could compete with the diffusion limited case. This could possibly be achieved by changing to a binding group with higher affinity toward the zinc porphyrin core. Alternatively a porphyrin with another transition metal could be used which would form a stronger bond to pyridine, e.g., ruthenium porphyrins.[40] This conclusion is based on the fact that the dissociation of the excited complex is slower than the actual energy transfer and is supported by previous observations of energy and electron transfer from ruthenium and zinc porphyrins to pyridine–fullerene ligands to occur before complex dissociation.[41]

The second observation is that in the case where the sensitizer triplet lifetime is short the diffusive energy-transfer efficiency decreases markedly. This would be the case when more oxygen is present in the sample, and if the energy transfer in a coordination complex is fast, sensitization of the annihilator would be efficient even in the presence of oxygen. However, to result in TTA-UC in ambient atmosphere the rate of the TTA process must also be increased and examples of self-oriented and supramolecular structures where this is observed have been presented recently.[23,24,42−46] Combining sensitizer–annihilator complexes in larger supramolecular structures with increased TTA rate could therefore lead to efficient TTA-UC, possibly functioning in air.

One important optimization required for coupled sensitizer–annihilator structures is the minimization of the detrimental singlet energy transfer from the singlet excited annihilator to the sensitizer.[25−28] In our sensitizer–annihilator complexes this occurs through FRET and is therefore distance and orientation dependent, as described in eqs 3 and 4.[37]

To reduce the quenching in a FRET pair, the distance, the orientation, or the spectral overlap can be optimized. Our choice of an axial ligand was based on the close to 90° angle between the annihilator and porphyrin transition dipole moments which would attenuate the energy transfer. However, in the annihilator–sensitizer complexes presented herein efficient energy transfer to the porphyrin was still observed. One reason is the quite flexible dynamic complexation which results in an apparent binding angle of 71–75°. A stronger binding constant could also lead to a binding angle closer to 90°, but a total elimination of FRET by only increasing the binding strength is not likely.

Instead one also has to engineer the spacing between the sensitizer and the annihilator as well as the spectral overlap. Here we have studied compounds spaced from 8 to 25 Å. Extending the arm much further than 25 Å will be challenging and possibly not viable for future applications. Not only does the desired triplet energy transfer through the bridge become less efficient over longer distances but also the synthetic route becomes more demanding. Unfortunately we were not able to distinguish between any triplet energy transfer through the bridge and that occurring by normal diffusive TET either by steady state or nanosecond transient absorption measurements (Supporting Information, Figure S32).

An alternative to extending the spacing between the annihilator and sensitizer would be to use a polymeric or oligomeric annihilator structure allowing triplet migration between annihilator units with subsequent TTA further away from the sensitizer. Systems displaying triplet migration between arranged annihilators have been demonstrated recently[23,24,42−46] and as discussed above would also benefit the TTA, possibly resulting in TTA-UC materials functioning in air equilibrated solutions.

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The spectral overlap integral, J, between the annihilators and the coordinated sensitizer is rather large in these systems, especially as coordination induces a red-shift in the ZnOEP absorption, and is determined to 1.16×10^{15} nm^4 M^{-1} cm^{-1}. This could be reduced substantially by either blue-shifting the porphyrin absorption by ∼20 nm or red-shifting the anthracene emission by a similar amount. We estimate the overlap integral to be reduced to 1/10 in such a case, resulting in a FRET efficiency, η_{FRET}, of 67% in the case of a 25 Å spacer, corresponding to the Ph_5AnPyr bridge. If this is combined with an orientation factor that is a tenth of that reported here for Ph_5AnPyr an η_{FRET} of 17% would be possible.

CONCLUSIONS

To conclude, we synthesized four 9,10-substituted anthracenes containing a pyridine substituent and assessed these pyridine-substituted anthracenes as annihilators in triplet−triplet annihilation upconversion (TTA-UC) systems. Using a zinc porphyrin (ZnOEP) as the sensitizer, we achieved the first sensitizer−annihilator coordination complex used for TTA-UC. We further studied the parasitic Förster resonance energy transfer from annihilator back to the sensitizer, which was found to be very efficient (>95%), contrary to what was previously observed for anthracene−Sn(IV) porphyrin systems.[29] Even though FRET was very efficient, upconverted emission was observed for all anthracene ligands.

From the findings here, we explore future design strategies for sensitizer−annihilator complexes. For one we propose that at least a 10 times stronger binding constant than the present 6000 M^{-1} would be necessary to achieve a reasonable sensitizer−annihilator complex concentration. We also suggest that sensitizer−annihilator coordination complexes can be beneficial in future supramolecular structures for TTA-UC functioning in air-equilibrated solutions or in solid matrices.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b06298.

Experimental procedures and characterization of new compounds as well as description of SVD analysis, corresponding spectroscopic data, time-resolved fluorescence, and transient absorption measurements (PDF)

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Notes

The authors declare no competing financial interest.

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