Determinants of the efficiency of photon upconversion by triplet-triplet annihilation in the solid state: zinc porphyrin derivatives in PVA

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Abstract

Spectroscopic, photophysical and computational studies designed to expose and explain the differences in the efficiencies of non-coherent photon upconversion (NCPU) by triplet-triplet annihilation (TTA) have been carried out for a new series of alkyl-substituted diphenyl and tetraphenyl zinc porphyrins, both in fluid solution and in solid films. Systematic variations in the alkyl-substitution of the phenyl groups in both the di- and tetraphenyl porphyrins introduces small, but well-understood changes in their spectroscopic and photophysical properties and in their TTA efficiencies. In degassed toluene solution TTA occurs for all derivatives and produces the fluorescent S\textsubscript{2} product states in all cases. In PVA matrices, however, none of the di-phenylporphyrins exhibit measurable NCPU whereas all the tetraphenyl-substituted compounds remain upconversion-active. In PVA the NCPU efficiencies of the zinc tetraphenylporphyrins vary significantly with their steric characteristics; the most sterically crowded tetraphenyl derivative exhibits the greatest efficiency. DFT-D computations have been undertaken and help reveal the sources of these differences.
Introduction

In spite of extensive, creative research in the field of solar photovoltaics (SPV), the efficiencies of single-junction SPV devices remain limited by the mismatch between the solar emission spectrum and the absorption spectrum/band gap of the materials employed.\textsuperscript{1-5} One of the cutting-edge efforts in SPV research therefore involves developing photon-managing processes that circumvent this fundamental limitation. Non-coherent photon upconversion (NCPU) by triplet–triplet annihilation (TTA) is one of the most promising of these avenues of research.\textsuperscript{1-13}

In the usual case, NCPU-TTA consists of a series of photophysical events beginning with the harvesting of low-energy photons by a sensitizer that undergoes efficient intersystem crossing (ISC) to its lowest triplet state. This is then followed by triplet–triplet energy transfer (TTET) to a non-absorbing but highly fluorescent acceptor with a long-lived triplet state and a large $S_1 - T_1$ energy gap. The triplet excitons thus produced diffuse during their lifetime, and a population of the fluorescent singlets can then be produced by means of TTA if they undergo short-range encounters. Upconverted (blue-shifted) emission results, but with a quantum efficiency that is often considerably less than 0.5 on a per absorbed photon basis.\textsuperscript{6,9,12}

In explorations of processes that might improve the overall efficiency of NCPU-TTA, our groups have shown that homo-molecular NCPU-TTA in molecules such as $d^0$ or $d^{10}$ metalloporphyrins (MPs) that have unusually long-lived second excited singlet ($S_2$) states may prove useful.\textsuperscript{5,14-17} Homo-molecular NCPU-TTA involves photoexcitation of the porphyrin in its Q band, which in MPs with extended $\pi$ electron systems can extend well into the near infrared. The first excited singlet state ($S_1$) thus formed then undergoes highly efficient ISC to the first excited triplet state, $T_1$, which in many MPs is intrinsically long-lived. Then, if two MPs in $T_1$ are
in close proximity, either by initial aggregation or by diffusion, they can annihilate to yield, preferentially, one MP in the ground $S_0$ state and one in the second excited singlet state singlet, $S_2$. Upconverted emission is then generated by radiative relaxation of $S_2$,\textsuperscript{15,16} which in monomeric MPs has an oscillator strength close to 1. The MP thus acts as dual absorber-upconverter, eliminating the TTET step. Although the quantum efficiency of ISC in MPs is close to 1, a small yield of fluorescence from $S_1$ remains as a convenient direct measure of the absorbed power.

A major impediment to the practical use of such a process is that the $S_2$ product state in MPs rapidly decays non-radiatively to $S_1$. As a result the $S_2$ fluorescence quantum yield is too small for the upconverted emission to be used directly in devices; this effect is particularly detrimental in Pt and Pd MPs, where $S_2$ lifetimes are so short that upconverted emission is essentially undetectable. Nevertheless, if ultrafast, efficient FRET or electron transfer from the $S_2$ state of a MP with a picosecond lifetime to another active element in an SPV could be arranged, the inherent efficiency of the homo-molecular NCPU-TTA upconversion process and the near infrared absorption of the substituted MPs would prove very useful. Both ultrafast electron transfer and resonant electronic energy transfer from the $S_2$ states of zinc MPs to suitable acceptors have been documented recently.\textsuperscript{18,19}

NCPU-TTA also requires its annihilating triplet states to live long enough to undergo bimolecular encounters, often under environmentally adverse conditions. Realizing efficient NCPU-TTA in the amorphous solid state is therefore much more difficult compared to fluid solution owing to restricted exciton diffusion rates. Developing NCPU-TTA systems that are functionally efficient under amicable device processing conditions, \textit{e.g.} in aerated, non-fluid, non-volatile media, is therefore highly desirable.
A variety of polymer blends, including polyurethanes, polyacrylates, polymethylmethacrylate, and polyphosphoesters, have been used as hosts for dopants that undergo NCPU-TTA in the recent past. The efficiencies of NCPU-TTA achieved in such amorphous matrices can be significant but are still not comparable to those observed in fluid solution. In addition, quenching of the triplets by oxygen can often limit the efficiency of NCPU-TTA in solid-state devices operating under aerated conditions. However, recent work by Kimizuka et al. is encouraging. In a series of reports this group have shown that TTA in doped metal-organic frameworks, in supramolecular organogel matrixes, in water and in polyvinyl alcohol (PVA) films can all proceed with high efficiency under aerated conditions.

All of these recent studies have employed donor-acceptor sensitized NCPU-TTA, leaving considerable scope for explorations of homo-molecular NCPU-TTA using new MPs acting as dual absorber-upconverters. In addition, the cumulative evidence described above clearly indicates the importance of spatial ordering and molecular aggregation in controlling UC efficiencies. Here we develop physical insight concerning how both of these factors affect UC efficiency by comparing the NCPU-TTA properties of four alkyl-substituted zinc porphyrin derivatives (Scheme 1) in degassed fluid toluene and in aerated PVA films. While these porphyrins have been reported in previous studies, the effects of steric bulk and the resulting differences in their aggregation-related NCPU-TTA efficiencies have yet to be explored. A computational investigation of model non-covalent dimeric aggregates of these compounds has also been carried out to assist in elucidating their observed TTA efficiency differences.
Scheme 1

The *meso*-substituted zinc porphyrins with di-substituted tert-butylphenyl and mesityl groups: Zn-tetra-(di-tert-butylphenyl)porphyrin (ZnTBP), Zn-tetramesitylporphyrin (ZnTMP), Zn-bis-(di-tert-butylphenyl)porphyrin (ZnDBP), Zn-bismesitylporphyrin (ZnDMP) and the reference compounds zinc tetraphenylporphyrin (ZnTPP) and zinc diphenylporphyrin (ZnDPP).

**Experimental**

**Materials**

Zn-tetraphenylporphyrin (ZnTPP) and Zn-diphenylporphyrin (ZnDPP) were purchased from Sigma Aldrich and Frontier Scientific, respectively, and were used as received. Zn-tetra-(di-tert-butylphenyl)porphyrin (ZnTBP), Zn-tetramesitylporphyrin (ZnTMP), Zn-bis-(di-tert-butylphenyl)porphyrin (ZnDBP), and Zn-bismesitylporphyrin (ZnDMP) were synthesized,
purified, and characterized as described in the Supplementary Information, using literature procedures.\textsuperscript{24-28}

PVA (average molecular weight 70000 Da) was purchased from Sigma-Aldrich. Toluene used for sample preparation was of spectroscopic grade and water was freshly collected from an ultrapure filtration system (Millipore, resistivity 18 MΩ/cm). The porphyrin-doped PVA films were prepared by dissolving 2 g of PVA in 30 ml of Millipore water and mixing it with the desired concentration of the MP in ethanol. This solution was spread in a polypropylene dish and dried at 60\(^\circ\) C. The average thickness of the resulting polymer film was approximately 0.2 mm.

Techniques

All experiments were carried out at 298 K. Absorption spectra were recorded using a Cary 6000i UV-Vis-NIR spectrometer operating in dual beam mode. Solution spectra were taken in 1.0 cm \(\times\)1.0 cm quartz cuvettes. Corrected emission spectra were obtained with a PTI QuantaMaster spectrofluorometer with a 0.4 cm \(\times\) 1.0 cm cuvette. \(S_1\) fluorescence quantum yields (\(\phi\)) were calculated using the relative approach, with ZnTPP in toluene (\(\phi_{\text{ref}} = 0.033\)) as the reference standard.\textsuperscript{29} TTA emission measurements were carried out with a custom-modified Spex Fluorolog spectrofluorometer using a 0.2 cm \(\times\)1.0 cm quartz cuvette and one of several cw solid-state lasers (561 nm and 532 nm; excitation spot sizes of 4 mm and 2 mm, respectively) as the excitation source. The power density delivered to the sample was varied by means of a series of calibrated neutral density filters. Emission was observed via the short path of the cuvette to minimize reabsorption and through a notch filter to eliminate excitation laser scatter.

Nanosecond fluorescence lifetimes were measured with a Ti:sapphire laser (Mira, Coherent), which provided mode-locked pulses in the 700 to 1000 nm range. The 76 MHz pulse
train was sampled using a pulse picker to provide excitation pulses at an acceptable repetition rate, and was frequency doubled using a second harmonic generator. An excitation wavelength of 400 nm was chosen for measuring fluorescence decays. The instrument response function (IRF) was measured at the excitation wavelength using a Ludox scatterer, yielding an IRF with a width of ca. 100 ps. Time-correlated single photon counting (TCSPC) was used to collect fluorescence at the magic angle, and decay curves were accumulated with a minimum of 10,000 counts in the peak channel. Time-resolved fluorescence decay curves were analyzed by deconvoluting the observed decay with the IRF to obtain the intensity decay function represented as a sum of discrete exponentials:

\[ I(t) = \sum_i a_i \exp\left( \frac{-t}{\tau_i} \right) \]  

(1)

where \( I(t) \) is the fluorescence intensity at time \( t \) and \( \alpha_i \) is the amplitude of the \( i \)th lifetime such that \( \sum_i \alpha_i = 1 \). The goodness-of-fit to the experimental data was evaluated by considering the reduced chi-squared values, and analyzing the statistical randomness of the weighted residuals.

**Computation details**

Calculations were performed using the Gaussian 09 program. All porphyrin monomer structures were optimized using density functional theory (DFT) at the B3LYP/6-31G(d) level, which is known to be adequate for predicting the molecular geometries of reasonably large molecules such as those examined here. While traditional DFT methods do not properly account for dispersion in non-covalently bound aggregates, several dispersion-corrected methods have been proposed to remedy this deficiency. The inclusion of an augmented damped R−6 dispersion term has proven to provide an effective approach to describing London forces, and the
DFT-D functional has been shown to perform very well for both covalent and non-covalent interactions.\textsuperscript{34-36} Therefore, the non-covalently bound dimeric porphyrin structures were determined by optimizing the aggregates at the B97D/6-31G(d,p) level. Slices of the intermolecular potential energy surfaces of these dimers were also scanned at the B97D/6-31G(d,p) level.

**Results and Discussion**

The spectroscopic and photophysical properties of the zinc porphyrin derivatives (Scheme 1) were investigated systematically in toluene and in PVA films, cast as described above, using steady-state and time-resolved fluorescence techniques.

**Studies in toluene**

The absorption spectra taken in toluene are shown in Figure S.I. 1 (cf. Supplementary Information), the emission spectra in Figure S.I. 2, and the photophysical data are summarized in Table 1. For convenience of comparison these data are presented as the tetraphenyl-substituted derivatives (group G1, including ZnTBP and ZnTMP) and the diphenyl-substituted derivatives (group G2, including ZnDBP and ZnDMP) with the unsubstituted ZnTPP and ZnDPP as the respective reference compounds. Comparisons of the absorption spectra reveal that no appreciable change results from substitution of the model compounds with either t-butyl or methyl groups, as expected. In group G1 all absorption bands are observed at their expected wavelengths,\textsuperscript{33, 37, 38} and those of G2, exhibit a blue shift compared to those of G1, also as expected (cf. Table 1). Upon direct excitation within the Soret band (\(\lambda_{ex} = 400\) nm for G1, and 390 nm for G2), the characteristic emission bands arising from both the \(S_2\) and \(S_1\) states are observed (cf. Figure S.I. 2). Note the increased intensities of the vibronic Q bands in group G1, possibly caused by increased
chromophore distortion on substitution. To verify that the observed fluorescence is not due to impurities, the corrected fluorescence excitation spectra were measured at both $\lambda_{em} = 440$ nm and 650 nm (Figure S.I. 3; cf. Supplementary Information). The individually normalized absorption and fluorescence excitation spectra exhibited satisfactory overlap for each compound, thus eliminating artefacts due to impurities in the synthesized materials.\textsuperscript{39}

Table 1: Spectroscopic and photophysical data for compounds in fluid toluene.

<table>
<thead>
<tr>
<th>Compd</th>
<th>Soret Band (nm)</th>
<th>Q (0,0) Band (nm)</th>
<th>$S_2$ em $\lambda_{max}$ (nm)</th>
<th>$S_1$ em $\lambda_{max}$ (nm)</th>
<th>$\tau_1 \pm \Delta$ (ns)</th>
<th>$\phi_1 \pm \Delta$ (ns$^{-1}$)</th>
<th>$k_r \pm \Delta$ (ns$^{-1}$)</th>
<th>$k_{nr} \pm \Delta$ (ns$^{-1}$)</th>
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<tbody>
<tr>
<td>ZnTPP</td>
<td>423</td>
<td>549</td>
<td>426</td>
<td>646</td>
<td>1.9 ± 0.1</td>
<td>0.033*</td>
<td>0.017 ± 0.003</td>
<td>0.489 ± 0.029</td>
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<tr>
<td>ZnTBP</td>
<td>424</td>
<td>550</td>
<td>426</td>
<td>648</td>
<td>2.1 ± 0.1</td>
<td>0.039 ± 0.006</td>
<td>0.018 ± 0.004</td>
<td>0.456 ± 0.026</td>
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<tr>
<td>ZnTMP</td>
<td>421</td>
<td>549</td>
<td>423</td>
<td>643</td>
<td>2.4 ± 0.1</td>
<td>0.032 ± 0.005</td>
<td>0.013 ± 0.003</td>
<td>0.401 ± 0.020</td>
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<tr>
<td>ZnDPP</td>
<td>412</td>
<td>538</td>
<td>418</td>
<td>630</td>
<td>2.3 ± 0.1</td>
<td>0.029 ± 0.004</td>
<td>0.013 ± 0.002</td>
<td>0.423 ± 0.021</td>
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</tr>
<tr>
<td>ZnDBP</td>
<td>413</td>
<td>539</td>
<td>419</td>
<td>631</td>
<td>2.4 ± 0.1</td>
<td>0.031 ± 0.005</td>
<td>0.013 ± 0.002</td>
<td>0.405 ± 0.020</td>
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</tr>
<tr>
<td>ZnDMP</td>
<td>411</td>
<td>538</td>
<td>417</td>
<td>629</td>
<td>2.3 ± 0.1</td>
<td>0.027 ± 0.004</td>
<td>0.012 ± 0.002</td>
<td>0.418 ± 0.021</td>
</tr>
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</table>

* standard\textsuperscript{29}
The photophysical data in Table 1 also indicate that the pattern of phenyl substitution on the porphyrin macrocycle and the presence of alkyl substitution on the phenyl groups have only small effects on the radiative and radiationless decay parameters of these compounds. Within the error limits of the lifetime ($\tau_1$) and quantum yield ($\phi_1$) measurements, only the small differences in the measured $S_1$ fluorescence decay times can be considered as statistically significant, and this leads to corresponding small differences in the rate constants for the radiative ($k_r$) and non-radiative ($k_{nr}$) decay of the $S_1$ states. Nevertheless, because short-range interaction is demanded in TTA, one might expect the upconversion efficiencies to be more substantially affected by substitutions that result in sterically-hindered bimolecular interactions.

To confirm that the zinc porphyrins in this study can act as dual absorber-upconverters in the NCPU-TTA process, degassed toluene solutions were excited with low power cw diode lasers in each porphyrin’s Q origin band; $\lambda_{ex} = 561$ nm (for G1), and 532 nm (for G2). The upconverted $S_2$ emission was collected using only an appropriate notch filter to reject scattered excitation light. To make quantitative comparisons of the unconverted emission relative intensities, the absorber concentrations were adjusted to maintain a Q (0,0) band absorbance of 0.10 for each compound. Figure 1 shows the power dependence of the UC emission intensity of ZnTMP and ZnDBP; data for the other compounds are illustrated in Figure S.I. 4 (cf. Supporting Information). The dependence of the UC emission intensity on the absorbed power density (the latter measured by the residual $S_1$ fluorescence emission intensity of each compound as a surrogate$^{17}$) is shown in the double logarithmic plots of Figure 2. Minimum least squares fits of tangents to the curves at low, medium and high power are shown in Figure 2. Slopes between 1 and 2 are obtained, diminishing with increasing absorbed power density in each case, as expected of TTA kinetics in fluid solution.$^{40, 41}$
Figure 1: Power dependent upconverted emission of (a) ZnTMP and (b) ZnDBP in degassed toluene.

Figure 2: Double logarithmic plot of the UC $S_2$ emission intensity versus the $S_1$ fluorescence intensity, which serves as a proxy for the absorbed power. (a) G1: i-ZnTPP, ii-ZnTBP, iii-ZnTMP. (b) G2: i-ZnDPP, ii-ZnDBP, iii-ZnDMP. $\lambda_{ex} = 561$ nm for G1 and $\lambda_{ex} 532$ nm for G2 at the same absorbance of 0.10.
A rough estimate of the relative yields of upconverted $S_2$ emission in these systems can be obtained by dividing the integrated areas of the UC spectra (Figs. 1 and S.I. 4) by the sample absorbance at the excitation wavelength when the same incident power is employed. This was done for both groups at several incident power densities. Figure 3 shows a typical data set (16.6 mW for G1 and 2.1 mW for G2 in this case), from which it is evident that ZnTMP and ZnDBP are the best upconverters in groups G1 and G2, respectively. As is well-known from photochemical studies, both the pattern of macrocycle substitution by the phenyl groups and the substitution of the phenyl moieties themselves with alkyl groups that act as impediments to free torsional motion can have substantial effects on the efficiencies of UC in these dual absorber-upconverter systems. We defer discussion of these differences until the calculations of the dimer potential surfaces have been presented.

Figure 3: Relative UC $S_2$ photon yields in degassed toluene solution at room temperature. (a) G1 and (b) G2, each separately normalized to the same sample absorbance and the same incident power at the excitation wavelength.
Studies in PVA films

In PVA films, the Soret absorption bands of all compounds (Figure 4) are substantially broadened and red-shifted compared to the solution phase. Broadening of the Soret absorption band is consistent with aggregation of these metalloporphyrins, as has been reported previously in poly(methylmethacrylate) films and in metal oxide films.\textsuperscript{14, 16} The pattern of broadening is consistent with excitonic splitting; fitting these spectra with multiple Gaussian profiles suggested that two bands centered at 413 nm and 435 nm characterized the Soret region in each case.\textsuperscript{45} The enhanced ‘intensity borrowing’ of the Q band from the Soret band has been attributed to B-Q coupling in J-aggregates.\textsuperscript{46} However, no significant change was observed in the emission profiles upon excitation within the Soret band region; both S\textsubscript{2} and S\textsubscript{1} emission were detected in all compounds.

Figure 4: Absorption spectra of (a) G1 and (b) G2 dual absorber-upconverters in PVA (0.1 wt.%).
The temporal $S_1$ fluorescence decays of these compounds in PVA, excited at 400 nm and monitored at 650 nm, can be satisfactorily fit with double exponential functions; the data are presented in Table 2. The longer decay times (ca. 2 ns) are very similar to the fluorescence decay times typical of zinc porphyrins in fluid hydrocarbons and therefore can be attributed to the monomeric form of the compound. The shorter, more abundant decay components are then attributed to aggregates formed in the PVA films. Decay times are generally reduced upon aggregation by the introduction of additional radiationless decay processes and are well-known for metalloporphyrins such as these.\textsuperscript{16} The data of Table 2 suggest that a large fraction of the metalloporphyrin solute is aggregated in the PVA matrices produced here. Under such circumstances, it is likely that aggregates larger than dimers will be present. Unfortunately, the data obtained to date does not allow one to quantitatively assess the extent of aggregation and we proceed on the assumption that the largest fraction of the aggregates will be dimeric.
Table 2: Parameters from double exponential fits of the time-resolved $S_1$ fluorescence decay of group G1 and G2 compounds in PVA films under aerated conditions at room temperature. $\lambda_{\text{ex}} = 400$ nm and $\lambda_{\text{em}} = 650$ nm.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\tau_1$ (ns)</th>
<th>$\alpha_1$</th>
<th>$\tau_2$ (ns)</th>
<th>$\alpha_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnTPP</td>
<td>0.5 ($\pm$ 0.1)</td>
<td>0.88</td>
<td>1.3 ($\pm$ 0.1)</td>
<td>0.12</td>
</tr>
<tr>
<td>ZnTBP</td>
<td>0.8 ($\pm$ 0.1)</td>
<td>0.88</td>
<td>2.3 ($\pm$ 0.1)</td>
<td>0.12</td>
</tr>
<tr>
<td>ZnTMP</td>
<td>0.9 ($\pm$ 0.1)</td>
<td>0.71</td>
<td>4.9 ($\pm$ 0.1)</td>
<td>0.29</td>
</tr>
<tr>
<td>ZnDPP</td>
<td>0.2 ($\pm$ 0.1)</td>
<td>0.78</td>
<td>2.8 ($\pm$ 0.1)</td>
<td>0.22</td>
</tr>
<tr>
<td>ZnDBP</td>
<td>0.3 ($\pm$ 0.1)</td>
<td>0.90</td>
<td>2.2 ($\pm$ 0.1)</td>
<td>0.10</td>
</tr>
<tr>
<td>ZnDMP</td>
<td>0.4 ($\pm$ 0.1)</td>
<td>0.89</td>
<td>1.8 ($\pm$ 0.1)</td>
<td>0.11</td>
</tr>
</tbody>
</table>

Several reports, including ones from our groups, have emphasized that the NCPU efficiencies of MPs in the solid state can be optimized by controlling the extent of aggregation and the relative spatial orientation of the aggregates formed. However, the choice of matrix and its permeability by oxygen are equally important. In the latter respect, the use of PVA should favour increased efficiency because of its demonstrated oxygen-barrier properties.

In experiments to induce NCPU-TTA using our dual absorber-upconverters in PVA films, the following observations were of importance. (i) Under aerated conditions and a broad range of excitation power densities, $S_2$ NCPU emission was observed only in the compounds of group G1 in PVA films. No significant $S_2$ emission was observed for the compounds of group G2 in PVA under similar excitation conditions (except for the wavelength). (ii) The intensities of NCPU in
the group G1 compounds in PVA films did not show any appreciable improvement when the films were degassed. (iii) An undoped PVA film, excited at the highest power possible with the two visible lasers, showed no emission at any wavelength, confirming that the observed emission in the doped films was in fact due to NCPU-TTA. (iv) Of considerable interest, no appreciable UC S2 emission could be observed under any excitation conditions from any of the compounds of group G2 in the PVA films (cf. Figure S5 in the Supplementary Information). The spectrum of NCPU S2 emission observed for compound ZnTMP in a PVA film is shown in Figure 5 and its intensity power-dependence plot is shown in Figure 6. (Note, during the time required to scan both the S1 and S2 emission range, the PVA films were visibly damaged by the excitation beam. To minimize this effect, only the S2 range was scanned, rapidly, for UC measurements on the films, and under these conditions, there was no observable damage. Because of this however, we report power dependence plots as a function of laser power rather than as a function of residual S1 emission as was done in solutions.) No significant change in the slope (1.4) of the power-dependency plot for ZnTMP was observed over the entire power range available. Similar experiments for ZnTBP yielded a value of the slope close to 1. The relative UC efficiencies of the group G1 compounds are shown in Figure 7, obtained at a constant incident power of 22.8 mW.
Figure 5: Power dependent NCPU-TTA emission of ZnTMP in PVA (0.01 wt.%).

Figure 6: Power dependence of UC emission intensity (Conditions the same as in Fig. 5).

Figure 7: Relative UC S$_2$ emission intensities of compounds in group G1 in aerated PVA films.

In advance of calculations that will provide some clarity, we note the following in respect of the above observations. (i) In PVA films some sort of pre-aggregation of the upconverting
species must occur if UC intensities are to be significant. (ii) Group G1 compounds with D$_{4h}$ macrocycle substitutional symmetry, provide measurable, sometimes very good, UC intensities, but compounds of group G2, with D$_{2h}$ substitutional symmetry, do not. (iii) PVA provides a good oxygen barrier over whatever interaction time is needed to allow TTA to occur in the group G1 compounds. (iv) The nature and/or site of alkyl substitution on the phenyl groups of group G1 have a significant effect on the relative intensities of UC.

**Computational results**

The DFT-optimized structures (in the gas phase) of the monomers of ZnTPP and ZnDPP, serving as proxies for the compounds of groups G1 and G2 respectively, are shown in Figures S.I. 6a and 6b. In both model compounds, the planes of the phenyl rings are at an angle of approximately 112° (or -68°) to the plane of porphyrin ring (cf. Fig. S.I. 6). These results are in good agreement with previous reports.$^{19,31-33,49}$

Several plausible structures of non-covalently bound dimers of these model metalloporphyrins were then used as starting points for optimization using the dispersion-corrected DFT functionals. The three dimer structures shown in Figure 8 – face to face (F – F), slipped, and head to tail (H – T) – were chosen as starting points for ZnTPP with D$_{4h}$ substituted macrocycle symmetry, whereas the six plausible input dimer structures shown in Figure 9 were chosen for ZnDPP of lower D$_{2h}$ substituted macrocycle symmetry. Computation then found the structure of each dimer that minimized the total energy of the system, constrained only by the requirement that the path to this minimum-energy structure be one of monotonically decreasing energy. Note that this procedure may not find the global minimum energy structure of each dimer, but may better replicate the conditions under which the dimers are being formed in the PVA matrix.
Figure 8: Schematic diagram of the input structures of ZnTPP dimers subjected to energy-minimization.

Figure 9: Schematic diagram of the input structures of ZnDPP dimers subjected to energy-minimization.
The energy-minimized output structures of the dimers obtained in this manner are shown in Figure 10 and, with one exception, are slipped structures derived from the input orientations. This result is consistent with the experimental spectroscopic data showing that J-type aggregates are formed in the PVA matrices. The only exception was the H – T (⊥) input structure of the ZnDPP dimer shown in Figure 9 which would not minimize computationally, almost certainly because all structurally variable paths from the starting structure were uphill in energy. Although it is not immediately apparent from these diagrams, the detailed structures clearly show that the zinc atoms of each porphyrin ring are significantly drawn out-of-plane compared to their input structures, as expected of dispersively-bound dimers. The effects of solvation (polarizability continuum model with methanol parameters) on the dimer structures were also investigated. As expected, all the dimers are stabilized by solvation (cf. Figure S.I. 7, Supporting information), but no significant change was observed in the optimized dimer structures.
Figure 10: Local energy-minimized structures of the dimers of (a) ZnTPP and (b) ZnDPP obtained at the B97D/6-31G(d,p) level in the gas phase.

Figure S.I. 7 (cf. Supporting Information) depicts the absolute energies of the dimers obtained by this local energy-minimizing method, and their relative energies are shown in Figure 11. Note that a single global minimum-energy structure for each dimer is not generally found by this computational method. In cases such as the FF (⊥) and Slipped (⊥) input structures of ZnDPP (cf. Figure 9) where it might be reasonably assumed that the same local minimum could be
obtained from the two different starting structures, each along paths of diminishing energy, the same output structures with the same energy were obtained (cf. Figure 10 b). However, these calculations demonstrate that several different locally-stable, slipped structures of similar energy can be formed with each of the ZnTPP and ZnDPP dimers. In all cases the local minima differ in energy by only small amounts, so thermal equilibrium at room temperature among different conformers might be possible if the barriers between the local minima are not impossibly high. However, in many cases the large-scale molecular motion needed to move from one local minimum to another suggests that thermal equilibrium may not be achievable among all conformers in PVA matrices.

Figure 11: Relative stabilities of the optimized local minimum-energy structures of the (a) ZnDPP dimers and (b) the ZnTPP dimers obtained at the B97D/6-31G(d,p) level in the gas phase.
In order to gain greater insight into the structures and binding energies of these dimers, the intermolecular potential energy of the most stable dimer of each group was calculated along a one-dimensional path, the inter-monomer Zn-Zn distance, leading to (and proceeding past) its local minimum. A section of the potential energy surface (PES) for the ZnDPP dimer along $r_{\text{Zn-Zn}}$ is depicted in Figure 12.

Figure 12: Potential energy of the dimer of ZnDPP as a function of intermolecular distance $r_{\text{Zn-Zn}}$ (see text) obtained by DFT calculation at the B97D/6-31G(d p) level. The solid curve is a simple Lennard-Jones function using the calculated binding energy and an average minimum Zn-Zn distance (see text). It illustrates the relative breadth of the calculated dimer binding potential.

The shape of this PES is in general accord with that expected for a dispersively-bound dimer. However, it is much broader than those of simple Lennard-Jones 6-12 potentials (cf. Figure
12) used to model the dispersive interactions between atoms and small molecules. Note as well the shallow double minimum feature in which the lowest energy minimum is located at \textit{ca.} 3.3 Å with a slightly higher energy one at \textit{ca.} 4.0 Å. The difference in energy between the two local minima is \textit{ca.} 0.003 Hartree (2 kcal/mol) and the barrier between the two is of about the same magnitude. This result is consistent with the data of Figure 11 and is also consistent with the common understanding that the binding energies of J aggregates in metalloporphyrins can be similar over a rather wide range of values of their slip parameters.

Finally, we present $r_{\text{Zn-Zn}}$ data in Table 3 similar to that derived from Figure 12 in order to address the important question of why the dimers of group G2 do not exhibit significant upconversion by TTA in the PVA matrices whereas those of group G1 do. We begin by noting that TTA is expected to proceed by the same mechanism in both sets of dimers. Short-range energy transfer by the Dexter (electron exchange) mechanism should prevail in all cases. The lifetimes of the triplet states of ZnTPP and ZnDPP are similar as are the lifetimes and fluorescence quantum yields of the TTA product $S_2$ states of their monomeric species.\textsuperscript{16} The similarities of these photophysical properties are reflected in the similar NCPU-TTA fluorescence intensities obtained for both groups G1 and G2 in fluid solution.
Table 3: Distance between the two Zn atoms ($r_{Zn-Zn}$) in the output structures of the porphyrin dimers obtained by optimization at the B97D/6-31G(d,p) level in the gas phase.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Input geometry</th>
<th>Output geometry</th>
<th>$r_{Zn-Zn}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnTPP</td>
<td>F-F</td>
<td>Slipped</td>
<td>3.23</td>
</tr>
<tr>
<td></td>
<td>Slipped</td>
<td>Slipped</td>
<td>4.65</td>
</tr>
<tr>
<td></td>
<td>H-T</td>
<td>Slipped</td>
<td>4.96</td>
</tr>
<tr>
<td>ZnDPP</td>
<td>F-F (∥)</td>
<td>Slipped</td>
<td>3.93</td>
</tr>
<tr>
<td></td>
<td>Slipped (∥)</td>
<td>Slipped</td>
<td>4.59</td>
</tr>
<tr>
<td></td>
<td>H-T (∥)</td>
<td>Slipped</td>
<td>4.11</td>
</tr>
<tr>
<td></td>
<td>F-F (⊥)</td>
<td>Slipped</td>
<td>3.20</td>
</tr>
<tr>
<td></td>
<td>Slipped (⊥)</td>
<td>Slipped</td>
<td>3.36</td>
</tr>
</tbody>
</table>

For the studies in PVA matrices we use the computational results on the model ZnTPP and ZnDPP species to provide insight, and assume that the minimum energy structures exhibiting the closest Zn-Zn approach will exhibit the greatest frontier molecular orbital overlap and hence the most efficient TTA. Note from Table 3 that the slipped dimers of ZnTPP and ZnDPP obtained from face-to-face starting geometries exhibit the smallest Zn-Zn distances and that these distances are almost identical (3.23 Å and 3.20 Å for ZnTPP and ZnDPP respectively). However, the one for ZnDPP is obtained directly only from an approach that places the pseudo-C₂ axes of the two monomers perpendicular to one another.
If, as expected, the Dexter mechanism applies to the TTA in all cases, the orientation of one face-to-face dimer relative to another at the same \( r_{\text{Zn-Zn}} \) should not make any significant difference to the upconversion efficiencies. All the electronic transitions involved in excitation, annihilation and emission in the molecules of both groups G1 and G2 possess macrocycle in-plane transition moments. Note as well that the lifetimes of the \( S_2 \) states of the ZnTPP and ZnDPP monomers in fluid solution are identical but so short (ca. \( 2 \) ps\textsuperscript{40, 41}) that significant diffusional separation of the interacting species following TTA cannot occur during the product \( S_2 \) state’s lifetime. Because this constraint applies equally to upconversion in both fluid solution and PVA matrices, it seems unlikely that self-quenching of \( S_2 \) in the perpendicularly oriented pair of monomers would play a role in frustrating net upconversion in ZnDPP but not in ZnTPP.

By elimination, the lack of NCPU-TTA in the ZnDPP group of dual absorber-upconverters must be due to the formation, in PVA, of populations of porphyrin monomers oriented and spaced in such a way that either efficient triplet exciton migration or efficient annihilation (or perhaps both) is frustrated in group G2 but not G1. The previous observation of negligible NCPU-TTA in surfactant-substituted ZnTPP derivatives oriented in Langmuir-Blodgett films\textsuperscript{16} demonstrates that such orientation requirements are general and not limited to the ZnDPP species. Here, the calculations presented above suggest that, even in the absence of an amorphous matrix, the aggregate potential surfaces possess a large number of local minima, and that dimers trapped in many of these local minima would require large amplitude molecular motion to access the global potential minimum. Owing to symmetry differences, the number of local minima for molecules of group G2 is larger than those of group G1, and in PVA such large amplitude motion would require crossing impossibly high barriers. The rate of TTA depends inversely on the exponential of the inter-molecular distance. However, trapping the slipped dimers in PVA matrices at those potential
minima where the inter-porphyrin distances lie at the larger limit of the distribution of $r_{Zn-Zn}$ shown in Table 3 (i.e. about 5 Å) compared with the distance at the minimum (i.e. about 3.2 Å) would reduce the TTA rate by no more than a factor of 4 if the smallest possible van der Waals spacing of ca. 2.5 Å = L is chosen for a calculation of the Dexter TTA rate (cf. Figure 12; $k_{TTA} \propto \exp\{-2r_{Zn-Zn}/L\}$). The actual difference in the NCPU intensities of groups G2 and G1 in PVA for comparable absorbance and incident power density (17 mW) is $\geq 20$ (compare Figures 5 and S.I. 5).

We thus must conclude that the PVA matrix itself provides much smaller populations of appropriately oriented and spaced dimers for the group G2 compounds compared with those for group G1. The rather large differences in the relative efficiencies of NCPU-TTA in PVA for the group G1 species (Figure 7) provide evidence that the populations of porphyrins with the appropriate intermolecular orientation can vary substantially even when the pendant phenyl group substituents and substitution pattern are quite similar. Within group G1, the unsubstituted ZnTPP species shows the least efficient NCPU-TTA in PVA, whereas the t-butyl-disubstituted derivative is about 7 times more efficient and the trimethyl-substituted derivative about 20 times more efficient. That is, the ZnTPP derivative with the most sterically-crowded substituent phenyl groups provides the most efficient upconversion in the PVA matrices. This observation, and the fact that all the group G2 compounds will be less sterically-crowded than the group G1 compounds suggest that the lowest-energy slipped dimeric structures needed for triplet exciton migration and annihilation are formed most abundantly in PVA when the degree of steric crowding on the periphery of the macrocycle is greatest.

While we are presently unable to provide complete molecular-level detail as to the nature of the interactions between the PVA matrix and the various MPs, we are nevertheless now in a
position to provide some reasoned speculation. Non-covalent coordination between alcohols and MPs is well-established.\textsuperscript{50} Binding by coordination between the non-bonding electrons of the oxygen atoms of PVA and the zinc atoms of the metalloporphyrins is therefore anticipated. Such interactions are expected to be weaker when the pendant phenyl groups on the porphyrins are more numerous (\textit{i.e.}, tetraphenyl weaker than diphenyl) and when the phenyl substituents and substitution pattern sterically frustrate the zinc-oxygen interaction. The compound ZnTMP with a trimethyl substitution pattern that forces the four phenyl groups into the most perpendicular orientations is thus expected to exhibit the weakest PVA-porphyrin interaction. By default, in the competitive minimum-energy seeking environment that prevails when the PVA matrix is forming from its aqueous solution, the slipped dimer conformations of the porphyrin needed for the most efficient triplet exciton migration and annihilation are expected to be formed in greater abundance.

**Conclusions**

Spectroscopic, photophysical and computational studies of the relative efficiencies of NCPU-TTA of several alkyl-substituted diphenyl and tetraphenyl zinc porphyrins in toluene and in PVA have revealed the following important information. (i) Under aerated conditions PVA provides an environment in which oxygen quenching of the porphyrin triplets is inhibited thus minimizing oxygen effects on the TTA efficiencies. (ii) In fluid degassed toluene solution, alkyl-substitution of the phenyl groups in both the di- and tetraphenyl porphyrins introduces small, but well-understood changes in their spectroscopic and photophysical properties. TTA efficiencies vary modestly from derivative to derivative, but NCPU occurs in all derivatives and produces the fluorescent \( S_2 \) product states in all cases. (iii) In PVA matrices, none of the di-phenylporphyrins exhibit measurable NCPU whereas all the tetraphenyl-substituted compounds remain
(iv) In PVA the NCPU efficiencies of the zinc tetrphenylporphyrins vary significantly with their steric characteristics; the most sterically crowded tetrphenyl derivative exhibits the greatest efficiency. (v) DFT-D computations reveal that trapping of dimeric aggregates in local potential minima at larger intermolecular spacings will be more statistically prevalent for the diphenyl dimers than for the tetrphenyl dimers, but such local trapping differences cannot account for the vast difference in NCPU efficiencies between the two groups of porphyrins in PVA. (vi) The absence of measurable NCPU in PVA for the diphenyl-substituted group is attributed to their substantially lower steric bulk, leading to stronger binding to the PVA matrix and significantly smaller populations of porphyrin aggregates promoting triplet exciton migration and annihilation.

We expect that these data will be useful in future designs of photovoltaic devices that seek to improve overall solar-to-electrical power conversion efficiencies through the use of NCPU by TTA.

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References


**Graphical Abstract**

Spectroscopic, photophysical and computational studies designed to expose and explain the differences in the efficiencies of non-coherent photon upconversion (NCPU) by triplet-triplet annihilation (TTA) have been carried out for a new series of alkyl-substituted diphenyl and tetraphenyl zinc porphyrins, both in fluid solution and in solid films.
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Title:
Determinants of the efficiency of photon upconversion by triplet-triplet annihilation in the solid state: zinc porphyrin derivatives in PVA

Date:
2017-09-14

Citation:
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