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Critical Sensitizer Quality Attributes for Efficient Triplet—Triplet Annihilation Upconversion with Low Power Density Thresholds

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ABSTRACT: Triplet—triplet annihilation upconversion (TTAUC) is a power density-dependent process where photons of low energy are transformed into high energy ones. The most important attributes of efficient TTAUC are quantum yield $\Phi_{\text{TTAUC}}$, power density threshold $I_{\text{th}}$ (photon flux at which 50% of $\Phi_{\text{TTAUC}}$ is achieved), and the upconversion shift of emitted photons (anti-Stokes shift). To date, approaches to balance these parameters have remained unclear. Herein, the cumulative effects of sensitizer triplet lifetime ($\tau_{\text{S}}$), sensitizer-annihilator triplet energy gap ($\Delta E_T$), and the total concentration of the sensitizer on the power density threshold at high TTAUC quantum yields is evaluated experimentally using Pt, Pd, and Zn tetraphenylporphyrin derivatives and a tetra-tert-butylpyrene annihilator, and by kinetic rate modeling. The results suggest that a large energy gap ($\Delta E_T \geq 4 k_{\text{B}} T$) and long sensitizer triplet lifetime make the triplet—triplet energy transfer (TTET) extremely efficient and allow the utilization of high sensitizer concentrations for low $I_{\text{th}}$. However, for large upconversion shifts, the triplet energy gap should be as small as possible. Smaller energy gap values result in slower forward TTET and faster reverse TTET, which together with high total sensitizer concentration can lead to a quenching of annihilator’s triplet state and therefore elevate the $I_{\text{th}}$. In this regard, low concentration of a sensitizer is beneficial, making sensitizers with high molar extinction coefficients preferential. Sensitizers with a long living triplet state and a high molar extinction coefficient can work efficiently and have low $I_{\text{th}}$ at 0 $k_{\text{B}} T$ or even negative $\Delta E_T$. Kinetic rate modeling further helps to optimize the parameters for best possible TTAUC performance. Thus, the findings of the study pave the way for the design of TTAUC systems with superior performance, such as high $\Phi_{\text{TTAUC}}$ at low excitation power densities with large anti-Stokes shift, for, for example, solar-driven photovoltaics, photocatalysis, bioimaging, and safe light-triggered drug-delivery systems.

INTRODUCTION

Photon upconversion based on triplet—triplet annihilation represents an attractive approach to turn the photons of higher wavelengths into lower ones by using noncoherent excitation sources.1–4 Nowadays, the method draws a lot of attention because of its broad applicability, spanning from organic electronics to bionanotechnology.4–6 The process relies on an interplay between two pairs of photoactive molecules, namely a sensitizer and an annihilator. After the photoexcitation of a sensitizer with photons of low energy, through the processes of triplet—triplet energy transfer (TTET) and triplet—triplet annihilation (TTA), the two annihilator triplet state molecules collide to generate one annihilator singlet state of high energy, which emits the upconverted photon (Scheme 1).9 Altogether, the TTAUC quantum yield ($\Phi_{\text{TTAUC}}$) is a product of five parameters:

$$\Phi_{\text{TTAUC}} = \frac{1}{2} \times f \times \Phi_{\text{ISC}} \times \Phi_{\text{TTET}} \times \Phi_{\text{TTA}} \times \Phi_{\text{fl}}$$

where $f$ is the statistical probability to obtain a singlet excited state after TTA, $\Phi_{\text{ISC}}$ is the intersystem crossing efficiency of a sensitizer, $\Phi_{\text{TTET}}$ and $\Phi_{\text{TTA}}$ are TTET and TTA efficiencies, and $\Phi_{\text{fl}}$ is the fluorescence quantum yield of an annihilator.

As is clear from Scheme 1, the TTA efficiency ($\Phi_{\text{TTA}}$) relies on the concentration of the generated annihilator triplet state, which makes TTAUC quantum yield ($\Phi_{\text{TTAUC}}$) dependent on the power density of the excitation source.10–12 Recently, the power density threshold ($I_{\text{th}}$), that is, the power density value at which $\Phi_{\text{TTA}}$ and therefore $\Phi_{\text{TTAUC}}$ equals to 50% of its maximum for the system under study, has been proposed as a TTAUC figure-of-merit.13–15 Together with $\Phi_{\text{TTAUC}}$, $I_{\text{th}}$ value is one of the crucial criteria for the selection of TTAUC sensitizer/annihilator pairs. Indeed, TTAUC systems with high $\Phi_{\text{TTAUC}}$ that can be obtained at low excitation power densities are of paramount importance, for example, for the next generation of organic electronics and prospective biomedical applications.
applications. While the way to control $\Phi_{\text{TTAUC}}$ seems to be straightforward, the methods to fine-tune the excitation power density threshold remain limited. This lack of proper methodology strongly hampers the development of TTAUC-based photon management approach toward high performance devices, for example, solar cells.

The expression for $I_{\text{th}}$ value was proposed by Monguzzi et al.:

$$I_{\text{th}} = \frac{k_{\text{TTA}}^2}{k_{\text{TTA}} \times \alpha(e) \times \Phi_{\text{TTTET}}}$$

where $k_0 = 1/\tau_0^6$ and represents the rate constant of all annihilator unimolecular and pseudo-first-order processes such as phosphorescence and quenching with, for example, oxygen ($\tau_0^6$ is phosphorescence lifetime of an annihilator), $\alpha(e)$ is a sensitizer absorption coefficient, and $k_{\text{TTA}}$ is second-order TTA rate constant.

On the basis of eq 2, one can easily modulate $I_{\text{th}}$ values by using long-living annihilators. However, only a few annihilators have both high fluorescence quantum yield ($\Phi_0^a$) and high singlet state formation probability via TTA (parameter $f$ in eq 1) that are critical for high $\Phi_{\text{TTAUC}}$ values.

In this respect, the sensitizer choice allows a higher degree of freedom. Up to now, a large variety of sensitzers has been used for TTAUC studies starting from heavy-atom-free molecules toward metalated porphyrinoids and even semiconductor nanocrystals. Therefore, we are striving to understand the pathways toward efficient TTAUC in terms of power density threshold through the prism of sensitizer properties.

## RESULTS AND DISCUSSION

### Sensitizers and Annihilators under Study

A set of metal complexes of 2-(3-[10,15,20-tris(3,5-dinitro-2,5,8,11-tetra-tert-butylphenyl)]porphyrin-5-yl)phenoxo)ethanol with Pt, Pd or Zn (i.e., PtTPPOH, PdTPPOH, ZnTPPOH) was used as sensitizers (Scheme 2). The substances possess drastically different physicochemical characteristics such as triplet lifetime ($\tau_T^0$), triplet energy level ($E_T^0$), $\Phi_{\text{ISC}}$ and molar extinction coefficient at excitation wavelength of 532 nm ($\epsilon_{\text{ex}}$). The last one is responsible for the different sensitizer concentrations ($S_0$) for ensuring identical absorption coefficient $\alpha(e)$ and laser power utilization for all three sensitizers. Therefore, the choice of porphyrins allowed us to follow the effect of sensitizer triplet lifetimes and energy levels and molar extinction coefficient together with total concentration of the sensitizer on $I_{\text{th}}$ and $\Phi_{\text{TTAUC}}$.

2,5,8,11-Tetra-tert-butylperylene (TBPer) was selected as the annihilator because of perylene’s long triplet lifetime, high fluorescence quantum yield, and moderately high triplet state energy (4 ms, 96%, and $\sim$1.54 eV, respectively). Moreover, the singlet state formation probability via TTA ($\text{parameter } f$) for perylene is approaching unity, while the tert-butyl substituents prevent an aggregation making TBPer one of the first-in-class annihilators.

Degassed poly(ethylene glycol)-200 matrix with 30 mM oleic acid (PEG-OA) was employed as the media for experiments. The degassed PEG protects the sensitizer/annihilator system from back oxygen diffusion and allows a moderate degree of mobility for triplet–triplet interactions (TTT and TTA), while OA represents a powerful scavenger for the residual trace oxygen.

### TTA and TTA Photophysics

To prove the ability of the sensitizers under study to serve as triplet energy donors, time-resolved phosphorescence quenching experiments with TBPer were performed. Efficient TTT occurred and Stern–Volmer constants ($K_{\text{SV}}$) and forward TTT rates ($k_{\text{FTTET}}$) were calculated (see ESI). $K_{\text{SV}}$ values were in agreement with the triplet lifetimes of the sensitizers. Short living PtTPPOH showed a Stern–Volmer constant of $\sim 3 \times 10^3$ M$^{-1}$, while the longer living sensitizers PdTPPOH and ZnTPPOH revealed higher values of $100 \times 10^3$ and $220 \times 10^3$ M$^{-1}$, respectively. On the other hand, PtTPPOH and PdTPPOH demonstrated higher forward $k_{\text{FTTET}}$ rate constants than did ZnTPPOH ($5 \times 10^3$ and $6.4 \times 10^5$ M$^{-1}$ s$^{-1}$ vs $2.2 \times 10^5$ M$^{-1}$ s$^{-1}$). This fact can be explained in terms of triplet energy gap values for the sensitizer/annihilator pairs ($\Delta E_T$) (Figure 1). Indeed, forward and reverse TTT rate constants ($k_{\text{FTTET}}$ and $k_{\text{RTTET}}$) are dependent on the energy gap value through Boltzmann equation.

$$k_{\text{FTTET}} = k_0 \times \frac{1}{1 + e^{-\Delta E_T/k_B T}}$$
to obtain at least 90% the di
Boltzmann constant, \( T \). The annihilator TBPer was used at a wavelength to utilize 90% of input power density. The sensitizers were adjusted to have OD = 1 at the excitation selectively excite the porphyrins. Concentrations of the continuous wave laser emitting at 532 nm was employed to measured for every sensitizer/annihilator pair. Nd:YAG annihilator triplet state.

di gap makes the forward (FTTET) step enthalpy-driven and diffusion-controlled, hence facilitating the population of annihilator triplet state.

Power density dependences of upconverted light were measured for every sensitizer/annihilator pair. Nd:YAG continuous wave laser emitting at 532 nm was employed to selectively excite the porphyrins. Concentrations of the sensitizers were adjusted to have OD = 1 at the excitation wavelength to utilize 90% of input power density. The annihilator TBPer was used at a fixed 3 mM concentration to obtain at least 90% \( \Phi_{\text{TTET}} \) for all TTAUC pairs. Quantum yields of TTAUC for all of the pairs were calculated by using Rhodamine 6G in ethanol as a reference.\(^{25}\)

Figure 2a clearly shows the strong and weak annihilation regimes, which is an integral feature of TTAUC process described by the equations:\(^{10,12}\)

\[
f_{\text{TTA}} = \frac{k_{\text{TTA}}[A^*_p]}{k_p + k_{\text{TTA}}[A^*_p]} \tag{5}
\]

\[
\Phi_{\text{TTA}} = 1 - \frac{f_{\text{TTA}} - 1}{f_{\text{TTA}}} \ln(1 - f_{\text{TTA}}) \tag{6}
\]

where \( f_{\text{TTA}} \) is the fraction of triplets decaying via TTA deactivation pathway.

It also should be noted that by solving eqs 5 and 6 in terms of power density (which affects the \( [A^*_p] \) parameter), one can find the value at which the yield of triplet–triplet annihilation \( \Phi_{\text{TTA}} \) reaches 0.5 of its maximum (see ESI) resulting in the refinement of eq 2:

\[
I_{\text{th}} = \frac{(k_p)^2}{k_{\text{TTA}} \times \alpha(\varepsilon) \times \Phi_{\text{TTET}}} \tag{7}
\]

Moreover, if we describe the system with \( \Phi_{\text{TTA}} \) close to its maximum (0.9), the scaling coefficient in eq 7 rises from 2.513 to as high as 36. These values were used to validate the data presented on Figure 2b. The estimated 50% and 90% threshold values from eq 7 agreed with the experimental results. It is good to remember that as both \( k_p \) and \( k_{\text{TTA}} \) are intrinsic annihilator properties, there is no need to consider these when comparing power thresholds for different sensitizers with slow \( k_{\text{RTTET}} \) (large \( \Delta E_f \)).

The upconversion yields and power density thresholds are collected in Table 1. The \( \Phi_{\text{TTAUC}} \) values are in good agreement with \( \Phi_{\text{ISC}} \) and \( \Phi_{\text{TTET}} \) efficiencies for these porphyrins. It is noteworthy that the obtained power density thresholds for the three porphyrin/annihilator pairs were obviously different (Figure 2, Table 1), which is not evident from eq 7. According to eq 7, the pair with lowest \( \Phi_{\text{TTET}} \) should have had the highest \( I_{\text{th}} \). In striking contrast, the pair with the longest living triplet state sensitizer and more than 0.99 \( \Phi_{\text{TTET}} \), namely ZnTPPOH/TBPer, shows the highest \( I_{\text{th}} \) value (258 mW/cm\(^2\)), while PtTPPOH and PdTPPOH sensitized upconversion systems revealed lower power density threshold values, that is, 168 and 50 mW/cm\(^2\). According to the equations, there should have been only a slight difference in \( I_{\text{th}} \) for all of the sensitizer/annihilator pairs since \( \Phi_{\text{TTET}} \) are close for all pairs studied.\(^{15}\)

One of the reasons for this discrepancy is the large difference in the sensitizer concentrations \([S_0]\) because of different \( \varepsilon_{532} \) of the porphyrins used in our study. Recently, Schmidt et al. have stressed that a too high sensitizer concentration can be detrimental for the upconversion efficiency regardless of improved power density utilization. At constant power density, the \( \Phi_{\text{TTA}} \) dependence on the sensitizer concentration appeared
to be parabolic. On the basis of that observation, one may expect that $\Phi_{\text{TTA}}$ for maximum for the systems with excessive sensitizer concentration will be reached at higher $I_{\text{th}}$ values, as follows from the eqs 5, 6, and 7.\textsuperscript{27,28}

In addition, triplet energy gap ($\Delta E_T$) is not identical for the porphyrin/TBPer pairs, resulting in different FTTET and RTTET rate constants (eqs 3 and 4). Together with an excess of sensitizer, the fast reverse energy transfer can lower the annihilator triplet state concentration, thus suppressing the annihilator TTA process. In good agreement with this, for the ZnTPPOH/TBPer pair, which had the highest sensitizer triplet state concentration, $I_{\text{th}}$ value is highest in the set. It is therefore clear that reverse TTET must be considered and more detailed description for the $I_{\text{th}}$ needs than the one given by eq 7. Especially considering that low $\Delta E_T$ could lead to higher upconversion shifts, which is one of the most desirable properties for TTAUC.

**Kinetic Rate Modeling.** To shed light on the obtained parameters, we have performed full TTAUC kinetic rate modeling taking into account the processes depicted on the Scheme 1 while varying the sensitizer properties (for details see ESI, page 14). Herein, we have utilized the approach proposed by Schmidt et al.,\textsuperscript{16} taking also into account reverse TTET rate constant and sensitizer concentration $[S_0]$. Equilibrium conditions have been applied to solve the set of equations:

$$\frac{dS^*_T}{dt} = -\frac{dS^*_T}{dt} = k_{\text{photon}}[S_0]\Phi_{\text{ISC}} - k_{\text{rad}}[S^*_T]$$

$$- k_{\text{FTTET}}[S^*_T][A_0] + k_{\text{RTTET}}[A^*_T][S_0]$$

$$- k_{\text{TTA}}[2[S^*_T]^2 + [S^*_T][A^*_T]] = 0$$

(8)

$$\frac{dA^*_T}{dt} = -\frac{dA^*_T}{dt} = k_{\text{FTTET}}[S^*_T][A_0] - k_{\text{rad}}[A^*_T]$$

$$- k_{\text{RTTET}}[A^*_T][S_0] - k_{\text{TTA}}[[A^*_T]^2 + [S^*_T][A^*_T]] = 0$$

(9)

Table 1. Characteristics of 2,5,8,11-Tetra-tert-butylperylene TTAUC Sensitized by Different Porphyrins

<table>
<thead>
<tr>
<th>sensitizer</th>
<th>$\Phi_{\text{ISC}}$</th>
<th>$\tau_s$, ns</th>
<th>$\epsilon_{\text{SU}}$, M$^{-1}$ cm$^{-1}$</th>
<th>$[S_0]$, mM</th>
<th>$E_{\text{fT}}$, eV</th>
<th>$\Delta E_T$, eV (kBT)$^2$</th>
<th>$k_{\text{TTET}}$, M$^{-1}$ s$^{-1}$</th>
<th>$\Phi_{\text{TTA}}$</th>
<th>$I_{\text{th}}$, mW/cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtPTPOH</td>
<td>1</td>
<td>0.061</td>
<td>$10^6$</td>
<td>100</td>
<td>1.84</td>
<td>0.3 (11.67)</td>
<td>$5 \times 10^7$</td>
<td>0.9</td>
<td>29</td>
</tr>
<tr>
<td>PtPTPOH</td>
<td>1</td>
<td>0.75</td>
<td>$1.9 \times 10^4$</td>
<td>52</td>
<td>1.76</td>
<td>0.22 (8.56)</td>
<td>$6.4 \times 10^7$</td>
<td>0.993</td>
<td>31</td>
</tr>
<tr>
<td>ZnTPPOH</td>
<td>0.75</td>
<td>11.0</td>
<td>$3.4 \times 10^3$</td>
<td>294</td>
<td>1.56</td>
<td>0.02 (0.78)</td>
<td>$2.2 \times 10^7$</td>
<td>0.9986</td>
<td>24</td>
</tr>
</tbody>
</table>

$\Phi_{\text{TTA}} = 2k_{\text{TTA}}[A^*_T]^{2} \times \Phi_{\text{A}}^{-1}$

(10)

where $k_{\text{rad}} = 1/\tau_s$ is the sensitizer’s triplet first-order decay constant, $[S_0]$ = total annihilator concentration, $[S^*_T]$ = sensitizer triplet state concentration, $[A_0]$ = total annihilator concentration, $[A^*_T]$ = annihilator singlet state concentration, $[A^*_T]$ = annihilator triplet state concentration, $k_{\text{photon}} = \Phi \times \epsilon'$ is the photon absorption rate (in s$^{-1}$) in which $\Phi$ is photon flux (in moles of photons dm$^{-2}$ s$^{-1}$) and $\epsilon' = ln 10 \times \epsilon$ (in M$^{-1}$ dm$^{-1}$).

For the modeling, the excitation light power was expressed in photon absorption rate (in s$^{-1}$). The photon absorption rate was recalculated into power density (mW/cm$^2$) or vice versa to compare the results of the modeling with the experimental data. TBPer triplet decay rate constant ($k_\text{d}$) of 250 s$^{-1}$ was utilized based on the literature data,\textsuperscript{29} diffusion constant $= 5 \times 10^{-6}$ s$^{-1}$, $\Phi_{\text{ISC}} = 1$, and the triplet–triplet annihilation rate constant ($k_{\text{TTA}}$) of $2.5 \times 10^7$ s$^{-1}$ ($0.5 \times k_\text{d}$) was employed for TTAUC simulations. Maximum $\Phi_{\text{TTA}}$ value of 32% was set to make calculations consistent with performed spectroscopy experiments. Further, photon rate threshold ($k_{\text{photon}}$) was calculated as a photon absorption rate resulting in 16% upconversion quantum yield, that is, 50% of $\Phi_{\text{TTA}}$ maximum.

**Effect of Sensitizer Lifetime and S/A Triplet Energy Gap on TTAUC Photon Rate Threshold.** First, the additive effect of sensitizer triplet lifetime ($\tau_s$) and S/A triplet energy gap ($\Delta E_T$) were examined to address the issue of photon absorption rate threshold. Sensitizer lifetime was varied from 50 μs to 20 ms and $\Delta E_T$ values from 12 to 0 kBT (Figure 3). Other parameters were kept constant.

In essence, sensitizers with triplet lifetimes shorter than 100 μs limit the possibility to use the TTAUC pairs with small $\Delta E_T$ (below 3 kBT) to achieve low $k_{\text{photon}}$. On the contrary, a long triplet lifetime of the sensitizer (>5 ms) is extremely beneficial for TTAUC process regardless of $\Delta E_T$ values in the simulated conditions, that is, 3 mM TBPer concentration and $[S_0] = 100$
μM (Figure 3b). Notably, sensitizers with triplet lifetimes longer than 1 ms allow an efficient TTET even with lower amount of annihilator (e.g., 500 μM) while keeping $k_{\text{photon(th)}}$ values in the minimum (Figure 3a).

Low annihilator concentrations make TTAUC pairs more sensitive to lower triplet energy gap values (below 2 $k_B T$, or 0.0514 eV). At small $\Delta E_T$, the reverse TTET process is not negligible. Excessive concentration of the sensitizer in the ground state can react with the triplet state of the annihilator, thus competing with annihilator’s TTA. At the same time, the sensitizer triplet−triplet annihilation competes with the forward TTET from sensitizer to the ground state annihilator resulting in a lower concentration of annihilator triplet state and high photon rate thresholds.$^{30,31}$

However, a great excess of the annihilator with respect to the sensitizer, for example, from 3 to 30 mM, makes FTETT more feasible even for the sensitizers with short living triplet states and small $\Delta E_T$, hence suppressing RTTET and resulting in lower $k_{\text{photon(th)}}$ values (Figure 3b,c). On the other hand, high $[A_0]$ leads to higher excimer state formation probability, which decreases $\Phi_a^x$ and makes TTAUC less efficient (eq 1). Furthermore, solubility issues with high amounts of annihilator may come into play, especially in polymers and nanocarriers.$^{7,32}$

It is further clear from Figure 3 that with high $\Delta E_T$ values ($\Delta E_T \geq 4 k_B T$) and $\tau_0^x$ above 200 μs, there are no additional benefits from even longer sensitizer triplet lifetimes.

**Effect of Sensitizer Concentration and Lifetime on TTAUC Photon Rate Threshold.** An increase in sensitizer concentration $[S_0]$ can improve the photon absorption rate threshold (eq 7) while keeping $\Phi_{\text{TAUC}}$ as high as possible. Indeed, a simultaneous increase in both $[S_0]$ and $\tau_0^x$ should result in a dramatic increase in the sensitizer triplet state concentration. As a consequence, a decrease in $k_{\text{photon(th)}}$ values can be achieved. Keeping this consideration in mind, the response of TTAUC photon rate threshold to the changes in $\tau_0^x$ and $[S_0]$ was simulated while keeping $\Delta E_T$ fixed.

Figure 4a shows the dynamics of $k_{\text{photon(th)}}$ with respect to sensitizer triplet lifetime and total sensitizer concentration at $\Delta E_T = 4 k_B T$. There is a slight improvement in photon rate threshold ($\approx 7.5$ vs $5 s^{-1}$) upon changing the sensitizer triplet lifetime from 50 μs to 20 ms at $[S_0] = 100 \mu M$. However, three-fold increase in $[S_0]$ results in substantial decrease of the photon rate threshold for both $\tau_0^x$ values ($\approx 3.36$ and 1.86 $s^{-1}$). This offers a way to further improve $k_{\text{photon(th)}}$. The same tendency occurs for simulations where $\Delta E_T = 10 k_B T$ and $7 k_B T$ were used (ESI). Albeit, the change in photon rate threshold with $\tau_0^x$ becomes negligible for all three $\Delta E_T$ values when the sensitizer lifetime exceeds 200 μs.

High triplet energy gaps $\Delta E_T > 4 k_B T$ considerably limit the upconversion shift of emitted photons. Thus, a situation where $\Delta E_T$ is close to $0 k_B T$ is of a special interest. Notably, in this case, the reverse TTET effect may not be neglected a priori and must be always taken into account together with the sensitizer total concentration. Hence, a precise analysis of the photon rate threshold behavior with respect to the variations in the sensitizer triplet state lifetime and its total concentration was performed at energy gaps of 1, 0, and $-0.8 k_B T$ (Figure 4b−d).

Our modeling revealed that the $k_{\text{photon(th)}}$ dependence on $[S_0]$ and sensitizer lifetime is a parabolic surface with a distinct minimum.$^{27}$ The minimum $k_{\text{photon(th)}}$ value depends strongly on the sensitizer triplet state lifetime in shorter photon rate threshold for longer living sensitizers. This is particularly true in the case of a large sensitizer concentration. The $k_{\text{photon(th)}}$ initially decreases as sensitizer concentration and triplet lifetime increase due to generation of higher sensitizer triplet state concentrations and hence increased annihilator triplet state concentration through FTETT. However, after reaching a minimum for $k_{\text{photon(th)}}$ with respect to the sensitizer concentration, a further increase in $[S_0]$ affects the $k_{\text{photon(th)}}$ values negatively. Overly high sensitizer concentrations quench the annihilator triplet states through reverse TTET process, thus increasing the apparent $k_0$ rate constant, which is crucial for low power density threshold (eq 7).

The effect of reverse TTET becomes more pronounced for smaller triplet state energy gaps. For example, in the case of the sensitizer with 100 μs triplet lifetime at $\Delta E_T = 1 k_B T$, the photon rate threshold of 17 $s^{-1}$ was reached at 167 μM sensitizer concentration. Meanwhile for $\Delta E_T = 0$ and $\Delta E_T = -0.8 k_B T$, the minimum $k_{\text{photon(th)}}$ value was 72 $s^{-1}$ and 295 $s^{-1}$ at $[S_0]$ of 41 μM and 13 μM, respectively. The $k_{\text{photon(th)}}$ values are higher and cannot be made smaller with larger sensitizer concentrations. This is in striking contrast with the scenario when a sensitizer with long living triplet state was simulated. The photon rate threshold dramatically improved with respect to the values obtained for short living sensitizers. Moreover, long living sensitizers allowed the utilization of higher total sensitizer concentration without a negative effect on the photon rate threshold. It is important to emphasize that sensitizers with longer living triplet lifetimes and negative $\Delta E_T$ values can work even better than a short living sensitizer with positive energy gaps. For long living sensitizers, the low photon rate thresholds can be reached at low $[S_0]$ concentrations even at negative triplet energy gaps. A precise analysis of the kinetic parameters for the sensitizer/annihilator pairs with $\Delta E_T$ close to $0 k_B T$ can be used to design functional and efficient TTAUC systems.

Further, we analyzed and compared the results of our simulations with our experimental data. First, we focused on the sensitizer/annihilator pair with the most unexpected result, namely ZnTPPOH/TBPer. Simulations performed at $\Delta E_T = 1 k_B T$ and $\Delta E_T = 0$ for a molecule with ZnTPPOH properties in...
the presence of 3 mM of the annihilator showed $k_{\text{photon(th)}}$ values of 2 s$^{-1}$ and 2.5 s$^{-1}$ that corresponded to 58 and 73 mW/cm$^2$, respectively (Figure 4b,c). These values disagree with the value of 260 mW/cm$^2$ obtained for ZnTPPOH experimentally. Even at $E_T = -0.5$ k$_B$T, the simulated $I_{th}$ for ZnTPPOH/TBPer is 112 mW/cm$^2$ (ESI). Only an energy gap of $-0.8$ k$_B$T ($-0.02$ eV) gives good agreement between the modeling and the experimental value. Taking this energy gap into account together with the 1.56 eV ZnTPPOH triplet state energy obtained from phosphorescence studies, TBPer triplet state energy of $\geq1.58$ eV was elucidated in PEG-OA mixture. This value is consistent with results of Northrop et al. and Hall et al. where 1.57 eV triplet energy for perylene was calculated.\textsuperscript{33,34} It also proves that efficient TTAUC process with high quantum yield is possible at negative $\Delta E_T$, even though careful kinetic analysis is needed to ensure lowest $I_{th}$ values by adjusting the concentrations.\textsuperscript{35,36} By using 1.58 eV TBPer triplet energy level, the energy gaps $\Delta E_T$ for PtTPPOH/TBPer and PdTPPOH/TBPer were calculated to be 10 k$_B$T and 7 k$_B$T, respectively. The experimentally determined porphyrin/TBPer energy gaps were used to simulate the threshold $I_{th}$. The values of 70 mW/cm$^2$, 56 mW/cm$^2$, and 255 mW/cm$^2$ were obtained for PtTPPOH, PdTPPOH, and ZnTPPOH, respectively, which are in agreement with the experimental data (Table 1).

To prove the fact that reverse TTET is responsible for the high $I_{th}$ value for ZnTPPOH/TBPer as predicted by our modeling, we have performed the power density dependence experiment with three-times lower ZnTPPOH concentration (OD$_{532} = 0.34$) keeping 3 mM TBPer concentration. In the absence of reverse TTET, one may expect a rise in $I_{th}$ value due to much lower optical density at the excitation wavelength and hence lower absorption coefficient $\alpha(\varepsilon)$ according to eq 7. Remarkably, for lower ZnTPPOH concentration, we obtained lower $I_{th}$ value (Figure 5), which is already comparable with $I_{th}$ of PtTPPOH/TBPer pair with large $\Delta E_T$. This photon rate threshold behavior of ZnTPPOH/TBPer is in agreement with the results obtained by using kinetic rate modeling (Figure 4c).

Indeed, high sensitizer triplet state concentration promotes the population of annihilator triplet state through FTTET. On the other hand, in the case of ZnTPPOH/TBPer pair, the reverse TTET is enthalpy-driven, and hence, higher annihilator triplet state concentration makes RTTET more favorable. This leads to even faster consumption of annihilator triplets.\textsuperscript{35} Consequently, the sensitizer triplet states recover and annihilate with each other with no desired upconverted light generation (Scheme 1).\textsuperscript{30,31} Altogether, this requires higher $I_{th}$ values to reach high $\Phi_{\text{TTAUC}}$ yields.

### CONCLUSIONS

Triplet–triplet annihilation upconversion systems with large anti-Stokes shift, high $\Phi_{\text{TTAUC}}$, and low power density thresholds are highly desired. In excellent agreement with previous studies, our results indicate that high energy gap between a sensitizer and an annihilator triplet states (more than 4 k$_B$T) makes forward TTET process enthalpy-driven and diffusion-controlled. This combined with high $\Phi_{\text{SACO}}$, long triplet lifetime, and high molecular extinction coefficient of a sensitizer at the excitation wavelength leads to high TTAUC yields and extremely low $I_{th}$ values without any negative effects of high sensitizer concentrations.

However, large anti-Stokes shift is almost impossible for sensitizer/annihilator pairs with high $\Delta E_T$. Even though there are sensitizers with thermally activated delayed fluorescence and strong singlet-to-triplet absorption bands that could solve this issue, their implementation in TTAUC is still limited due to the reverse ISC process.\textsuperscript{37–39} Thus, S/A pairs with low $\Delta E_T$ must be used to increase the upconversion shifts. In this case, reverse TTET can be controlled via total sensitizer concentration in the system. This is of vital importance for systems utilizing low viscosity medium and annihilators with long living triplet lifetimes, which are more sensitive to a reverse TTET process (see ESI). Hence, preference should be given to the sensitizers with higher molar extinction coefficients and longer triplet lifetimes to neglect the effect of reverse TTET on $I_{th}$. Moreover, sensitizers with long living triplet states are capable of performing efficient upconversion even at negative triplet energy gaps. Finally, kinetic rate modeling is a powerful tool in the optimization of power density thresholds and upconversion quantum yields by manipulating the concentrations of sensitizer and annihilator.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.9b08026.

Synthetic procedures and compounds characterization, details of photophysical measurements and calculations (PDF)

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#### Notes

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REFERENCES


