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### Citation

Durandin, N. A., Isokuortti, J., Efimov, A., Vuorimaa-Laukkanen, E., Tkachenko, N. V., & Laaksonen, T. (2018). Efficient photon upconversion at remarkably low annihilator concentrations in a liquid polymer matrix: when less is more. *Chemical Communications*, 54(99), 14029-14032. <https://doi.org/10.1039/c8cc07592a>

### Year

2018

### Version

Peer reviewed version (post-print)

### Link to publication

[TUTCRIS Portal \(http://www.tut.fi/tutcris\)](http://www.tut.fi/tutcris)

### Published in

Chemical Communications

### DOI

[10.1039/c8cc07592a](https://doi.org/10.1039/c8cc07592a)

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## Efficient photon upconversion at remarkably low annihilator concentrations in liquid polymer matrix: when less is more

Received 00th January 20xx,  
Accepted 00th January 20xx

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DOI: 10.1039/x0xx00000x

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**Green-to-blue triplet-triplet annihilation upconversion of 24.5% quantum yield was achieved at a remarkably low 600  $\mu\text{M}$  annihilator concentration in viscous polymer matrix. This was made possible by utilizing a ZnTPP-based photosensitizer with exceptionally long 11 ms phosphorescence lifetime. Higher 3 mM annihilator concentration resulted in lower 24% upconversion quantum yield.**

Discovered by Parker and Hatchard in 1960's,<sup>1–3</sup> triplet-triplet annihilation-based photon upconversion (TTAUC) experiences a resurrection nowadays, as it is able to convert low-energy photons into high-energy ones under non-coherent, low-power excitation light.<sup>4</sup> Thus, the principle can be employed in numerous imperative applications including TTAUC-employed solar cells,<sup>5–7</sup> photocatalysis,<sup>8</sup> bio-imaging<sup>9,10</sup> and phototriggered drug delivery systems.<sup>11–14</sup>

To initialize TTAUC, a photo-excited sensitizer (S) molecule in its triplet state undergoes triplet-triplet energy transfer (TTET) to another molecule, called annihilator (A). Eventually, two annihilator triplets collide with each other to generate one singlet and one ground state via triplet-triplet annihilation (TTA). Consequently, the annihilator singlet state emits the photon of higher energy (lower wavelength) than the one absorbed by sensitizer, thus generating delayed upconverted fluorescence.<sup>1–3</sup> Thus the TTAUC efficiency depends on four parameters: intersystem crossing efficiency of a sensitizer ( $\Phi_{ISC}$ ), TTET and TTA efficiencies ( $\Phi_{TTET}$  and  $\Phi_{TTA}$ ), and quantum yield of annihilator fluorescence ( $\Phi_{fl}^A$ ) and can be expressed as follows:

$$\Phi_{UC} = \Phi_{ISC} \times \Phi_{TTET} \times \Phi_{TTA} \times \Phi_{fl}^A \quad (1)$$

Up to now most commonly used TTAUC sensitizers are noble metal porphyrins, such as Pt(II), Pd(II) complexes because of their high intersystem crossing efficiency ( $\Phi_{ISC} \geq 0.99$ ).<sup>4,15,16</sup>

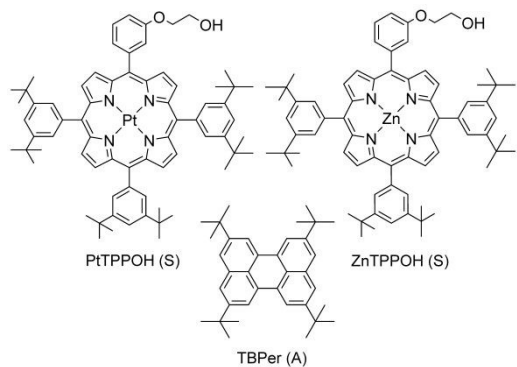
However, a vast majority of those sensitizers have rather short-living triplet states (up to several hundreds of microseconds), which is detrimental for the initial triplet-triplet energy transfer of TTAUC. Moreover, the rate of the triplet-triplet energy transfer is diffusion-limited and thus viscosity-dependent, which makes it a “bottleneck” for the whole TTAUC in polymeric matrices. A higher concentration of the annihilator makes TTET process more efficient, but on the other hand results in undesired aggregates and excimer formation.<sup>17,18</sup> This results in a decrease in TTAUC efficacy. Moreover, for soft matter systems high annihilator concentration is extremely challenging or unfeasible.<sup>11,12,19–22</sup> Thus, it is of paramount importance to find sensitizers with long living triplet state and high  $\Phi_{ISC}$  to overcome the problems mentioned above.<sup>23,24</sup>

Herein we used zinc tetraphenylporphyrin derivative, namely, zinc complex of 2-{3-[10,15,20-tris(3,5-di-tert-butylphenyl)porphyrin-5-yl]phenoxy}ethanol (ZnTPPOH), which takes advantage of the properties of ZnTPP ( $\Phi_{ISC} \approx 0.83$ – $0.88$ <sup>25,26</sup> and  $\tau_T \approx 4$  ms),<sup>27</sup> whilst the tert-butyl substituents prevent aggregation.<sup>26,27</sup> It is noteworthy that despite the promising properties of the ZnTPP molecule for TTAUC, quantitative data about ZnTPP-sensitized upconversion remains scarce.<sup>30–32</sup> However, there are a few studies on other Zn-containing porphyrins such as ZnTPTBP<sup>33</sup> and ZnOEP.<sup>34,35</sup>

In contrast to ZnTPPOH, Pt(II) complex of the same porphyrin (PtTPPOH) with  $\Phi_{ISC} \approx 1$  was also utilized as a sensitizer.<sup>36</sup> The use of PtTPPOH is rationalized here as a control molecule with a very similar structure to ZnTPPOH, but with shorter lifetime. In this way, it is possible to evaluate the effect of triplet state lifetimes on the efficiency of TTAUC. 2,5,8,11-Tetra-tert-butylperylene (TTBPer) was chosen as the annihilator because of perylene's ability to generate the singlet excited state with unity efficiency via TTA. Perylene also has a low enough triplet energy level for efficient TTET.<sup>37</sup> PtTPPOH and ZnTPPOH were prepared by a previously described method<sup>29</sup> and comprehensively characterized (see ESI), while TTBPer was purchased from a commercial source (Scheme 1).

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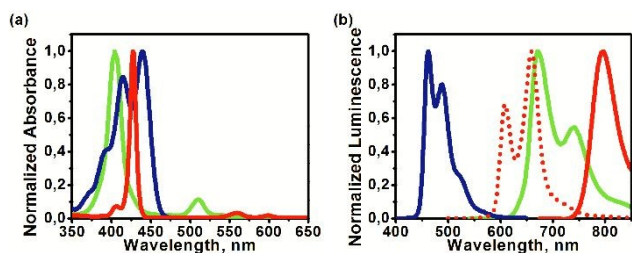
†Electronic Supplementary Information (ESI) available: Synthetic procedures and additional characterization results. See DOI: 10.1039/x0xx00000x



**Scheme 1** Molecular structures of PtTPPOH, ZnTPPOH and TTBPer.

Although most studies focus on performing the TTA experiments in organic solvents<sup>38–44</sup>, the sensitizer/annihilator pairs should actually be incorporated in a polymer matrix to anticipate their potential utilization in real applications. In the current study, we introduced our molecules into poly(ethylene glycol) 200 matrix doped with 30 mM oleic acid (PEG-OA) to simulate e.g. soft matter/polymeric device conditions. PEG-OA has been proposed by Castellano and co-workers<sup>45</sup> as a promising medium for TTAUC-based devices due to the low solubility of O<sub>2</sub> in PEG and the prominent oxygen scavenging properties of OA that are both essential for reducing losses associated with oxygen quenching of the triplet state.<sup>46–48</sup>

Figure 1 depicts the absorption and luminescence spectra of all three molecules in degassed PEG-OA matrix. It is noteworthy that in parallel with phosphorescence at 796 nm, ZnTPPOH exhibits pronounced fluorescence ( $\lambda_{\max}$ =660 nm) as a result of non-unity intersystem crossing efficacy of the ZnTPP moiety.<sup>25</sup>

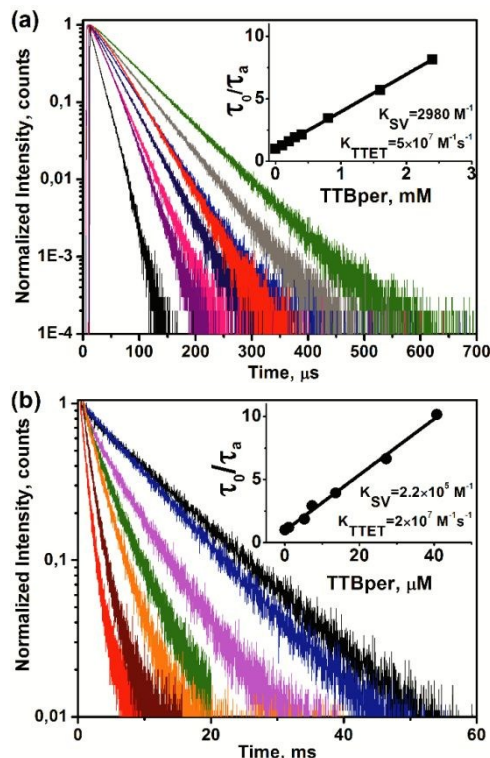


**Fig. 1** (a) Normalized absorption and (b) phosphorescence spectra of PtTPPOH (green), ZnTPPOH (red), and TTBPer (blue) in optically dilute (OD≈0.1) PEG-OA solutions. Dashed red line on 1b) is the fluorescence spectrum of ZnTPPOH.

Phosphorescence lifetime measurements of the porphyrins in degassed PEG-OA were conducted, followed by quenching experiments with TTBPer. Consequently, Stern-Volmer constants ( $K_{SV}$ ) and TTET rates ( $K_{TTET}$ ) were estimated (Figure 2; eq. 1 in ESI). Intact phosphorescence lifetime of ZnTPPOH shows dramatic difference of more than 2 orders of magnitude in respect to PtTPPOH. Due to the ultralong 11.0 ms triplet lifetime, the Stern-Volmer constant for ZnTPPOH is about 74 times larger than that for PtTPPOH ( $2.2 \times 10^5 \text{ M}^{-1}$  vs  $2980 \text{ M}^{-1}$ ). However,  $K_{TTET}$  is smaller for ZnTPPOH than for PtTPPOH ( $2 \times 10^7$  vs  $5 \times 10^7$

$\text{M}^{-1}\text{s}^{-1}$ ) which can be explained by the smaller triplet energy gap for ZnTPPOH/TTBPer pair in respect to PtTPPOH/TTBPer.

**Fig. 2** Time-resolved phosphorescence decays of PtTPPOH (a)



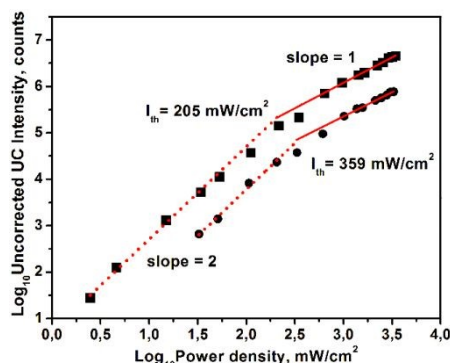
and ZnTPPOH (b) excited at 510 nm and 560 nm, respectively, with Xe  $\mu\text{F}$  flash lamp at different TTBPer concentrations. Insets: Corresponding Stern-Volmer plots for the set of concentrations used, where  $\tau_0$  and  $\tau_a$  are sensitizer triplet lifetime in absence and presence of particular annihilator concentration.

Based on the phosphorescence lifetime experiments, TTBPer concentration of 3 mM was chosen for further studies. At this concentration, more than 90% TTET efficiency ( $\Phi_{TTET}$ ) was obtained for both sensitizers. All the solutions were adjusted to have optical densities of 1.0 at the excitation wavelength to utilize 90% of the laser power density. This corresponds to the PtTPPOH and ZnTPPOH concentrations of 100  $\mu\text{M}$  and 294  $\mu\text{M}$ , respectively, according to the molecular extinction coefficients ( $\epsilon$ ) of PtTPPH ( $10^4 \text{ M}^{-1}\text{cm}^{-1}$ ) and ZnTPPOH ( $3.4 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$ ) at 532 nm.

To our delight, selective excitation of porphyrins at 532 nm by using second-harmonic Nd:YAG laser in presence of TTBPer gave a rise to an anti-Stokes blue emission at 460 nm (see ESI). The intensity of the upconverted light was measured as a function of laser power density resulting in quadratic-to-linear power dependence (Figure 3), which corresponds to the annihilation nature of the blue fluorescence. At low power densities (slope = 2) non-radiative triplet decay contributes more to the kinetics of the process. Above the power threshold point ( $I_{th}$ ) TTA starts to dominate, approaching a maximum for UC fluorescence (slope = 1).<sup>50</sup> The  $\Phi_{UC}$  values of 29% and 24% for PtTPPOH/TTBPer and ZnTPPOH/TTBPer pairs, respectively, were calculated from the data. The difference in values is

related to the difference in  $\Phi_{ISC}$  for the corresponding porphyrins.<sup>51</sup>

**Fig. 3** Double logarithmic plot of the upconverted emission for



PtTPPOH/TTBPer (squares) and ZnTPPOH/TTBPer (circles) as a function of power densities.

As the Stern-Volmer constant for ZnTPPOH was so high, we were encouraged to investigate the effect of annihilator concentration on UC intensity at constant sensitizer concentration and high power density (3300 mW/cm<sup>2</sup>). Triplet-triplet energy transfer efficiency ( $\Phi_{TET}$ ) reached 91% already at 50  $\mu$ M concentration of the annihilator, and this process has almost no effect on TTAUC efficiency ( $\Phi_{UC}$ ) at higher TTBPer concentrations. At low annihilator concentrations (below 0.1 mM), the observed quadratic dependence of UC intensity, and thus  $\Phi_{UC}$ , indicates the prevalence of unimolecular and pseudo-first-order annihilator triplet deactivation pathways. However, this is not the case for annihilator concentrations higher than 100  $\mu$ M. Linear dependence means that TTA is already a dominant mechanism of TTBPer triplet degeneration in the system. Further increase in the annihilator concentration resulted in plateau thus  $\Phi_{TTA}$  and consequently whole TTAUC ( $\Phi_{UC}$ ) reached its maximum (equation 1). In essence, 600  $\mu$ M and 1.5 mM of TTBPer were enough to obtain  $\Phi_{UC}$  of 24.5% and 26.4%, respectively (Figure 4a).

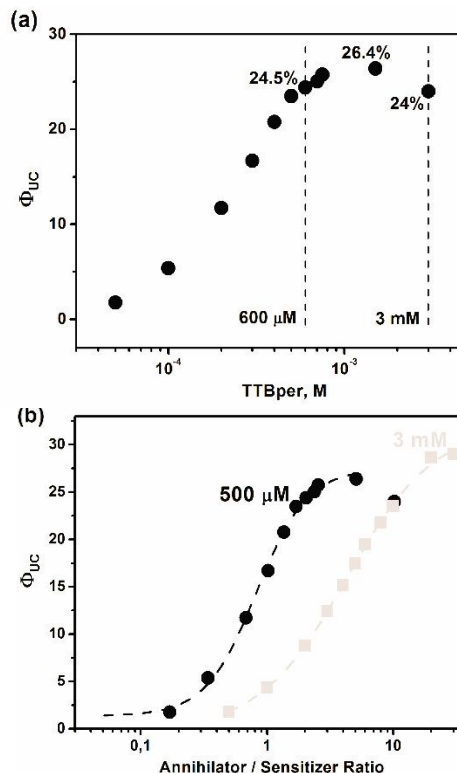
It is worth mentioning that a higher TTBPer concentration (3 mM) resulted in lower  $\Phi_{UC}$  (24%). This can be attributed to the fact that higher TTBPer concentration leads to higher probability of excimer formation. Thus, the quantum yield of monomeric annihilator fluorescence ( $\Phi_{fl}^A$ ) decreases resulting in lower  $\Phi_{UC}$ .<sup>37</sup>

Consequently, TTAUC sensitization property of ZnTPPOH has been compared with PtTPPOH. Since  $\epsilon_{532}$  of ZnTPPOH and PtTPPOH are substantially different resulting in prominent concentration inequality at identical optical density the annihilator/sensitizer ratio (An/Sen) has been employed to compare obtained results. Figure 4b clearly demonstrates the benefits of ZnTPPOH utilization for TTAUC in the An/Sen range i.e. from 0.5 to 3. Indeed, when PtTPPOH was able to generate only 4.4% of  $\Phi_{UC}$  ZnTPPOH has already sensitized TTAUC with more than 16.5% quantum yield.

In summary, we report ZnTPP-based photosensitizer possessing to our knowledge the longest triplet lifetime (11 ms) among the sensitizers used for TTAUC together with high  $\Phi_{ISC}$  of

0.75. In the case of ZnTPPOH, this allows us to perform TTET in more efficient way by using a lower amount of the annihilator in comparison with widely used expensive Pt(II) porphyrins. As a result, TTAUC with 24.5%  $\Phi_{UC}$  has been obtained by using only 600  $\mu$ M of TTBPer even in a viscous polymer matrix. This is in striking contrast with 3 mM annihilator concentration needed for PtTPPOH-sensitized photon upconversion with 29% TTAUC efficiency.

**Fig. 4** (a) A plot of the TTAUC quantum yield in respect to the molar



concentration of TTBPer used upon excitation of ZnTPPOH at 532 nm; (b) Dependence of  $\Phi_{UC}$  in respect to the An/Sen ratio upon excitation of ZnTPPOH (circles) and PtTPPOH (squares) at 532 nm.

This demonstrates that looking for molecules with long-living triplet lifetimes and high  $\Phi_{ISC}$  would be extremely important whenever efficient TTAUC is needed, especially in viscous media. Moreover, we stress that overly high annihilation concentrations are deleterious for TTAUC. Our results clearly prove that at lower TTBPer concentrations  $\Phi_{UC}$  is higher to some extent. This finding can be useful in a variety of applications, such as sensors, photocatalysis, photovoltaics, and phototriggered drug delivery systems, where the high loading of the molecules is difficult, but high  $\Phi_{UC}$  value is still desired.

This work was supported by The Academy of Finland (grant number 316893), fellowship programme of the Centre for International Mobility, (CIMO, decision TM-16-10063, Finland).

## Conflicts of interest

There are no conflicts to declare.

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DOI: 10.1039/C8CC07592A