

# Efficient Triplet–Triplet Annihilation Upconversion in Solution and Hydrogel Enabled by an S-T Absorption Os(II) Complex Dyad with an Elongated Triplet Lifetime

Yaxiong Wei, Yuanming Li, Zefeng Li, Xinsheng Xu, Xiaosong Cao,\* Xiaoguo Zhou,\* and Chuluo Yang\*

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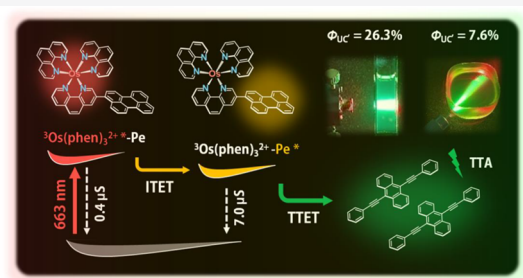
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**ABSTRACT:** A new Os(II) complex dyad featuring direct singlet-to-triplet (S-T) absorption and intramolecular triplet energy transfer (ITET) with lifetime up to 7.0  $\mu$ s was designed to enhance triplet energy transfer efficiency during triplet–triplet annihilation upconversion (TTA-UC). By pairing with 9,10-bis(phenylethynyl)anthracene (BPEA) as a triplet acceptor, intense upconverted green emission in deaerated solution was observed with unprecedented TTA-UC emission efficiency up to 26.3% (with a theoretical maximum efficiency of 100%) under photoexcitation in the first biological transparency window (650–900 nm). Meanwhile, a 7.1% TTA-UC emission efficiency was acquired in an air-saturated hydrogel containing the photosensitizer and a newly designed hydrophilic BPEA derivative. This ITET mechanism would inspire further development of a highly efficient TTA-UC system for biological fields and renewable energy production.



## INTRODUCTION

Triplet–triplet annihilation upconversion (TTA-UC) has attracted increasing attention because of its occurrence with low excitation power density, noncoherent incident light, high TTA-UC emission efficiency ( $\eta_{UC}$ , the theoretical maximal efficiency being 100%), and adjustable absorption/emission wavelength.<sup>1,2</sup> These features render TTA-UC applicable in vast fields including photovoltaics, photocatalysis, H<sub>2</sub> gas production, and bioimaging.<sup>3–8</sup> In particular, the TTA-UC of photoexcitation in the first biological transparency window (650–900 nm)<sup>9–11</sup> is highly desirable in bioimaging because of the good tissue penetration of the low-energy excitation light.<sup>12</sup>

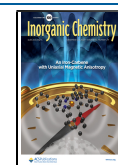
A triplet energy donor (photosensitizer) and energy acceptor (triplet annihilator/emitter) are key components in typical TTA-UC systems.<sup>13,14</sup> Owing to highly efficient intersystem crossing by strong spin-orbit coupling (SOC), photosensitizers typically employ transition metals (Pt, Pd, Ru, and Ir) or heavy atoms (I and Br) to populate triplet excitons.<sup>15–17</sup> In recent years, some pure organic photosensitizers have also been developed for TTA-UC including thermally activated delayed fluorescence materials, fullerene (C<sub>60</sub> and C<sub>70</sub>) derivatives, and spin-orbit charge transfer intersystem crossing molecules.<sup>18–22</sup> Nonetheless, the absorption bands of most photosensitizers are mainly distributed in the visible region, and TTA-UC pairs that are able to convert light from deep-red (>650 nm)/near-infrared (NIR) to visible region remain scarce (Table S1).<sup>1</sup>

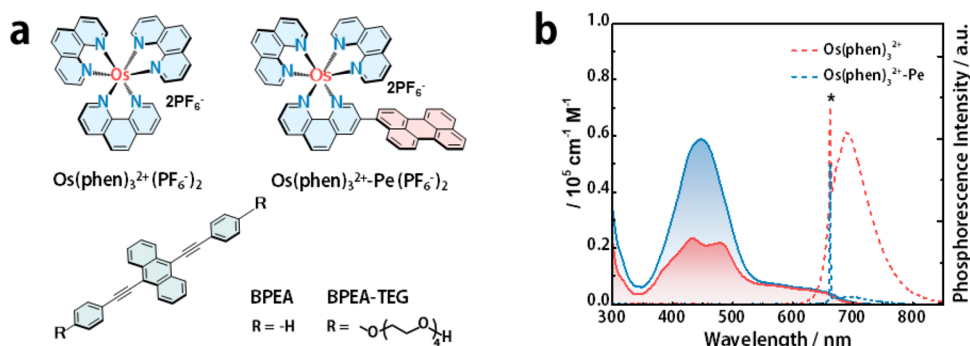
Pt(II)/Pd(II) porphyrin derivatives are classical triplet energy donors with deep-red/NIR absorption, but the complex synthetic protocols and inferior upconversion efficiency (typically below 20%) hinder their applications.<sup>23–25</sup> Lately, Kimizuka et al.<sup>26,27</sup> developed a series of new photosensitizers enjoying direct singlet-to-triplet (S-T) excitation. The S-T absorption compounds exhibit a sufficiently large absorption coefficient from the ground state (S<sub>0</sub>) to the lowest excited triplet state (T<sub>1</sub>) state due to significant SOC. In this way, these triplet photosensitizers can circumvent the energy loss of intersystem crossing, and the absorption band could be easily extended to a long-wavelength region. Nonetheless, the fast deactivation of the triplet excited state caused by strong SOC is detrimental to the triplet energy transfer process to the acceptor. For instance, in our previous attempt to apply an S-T absorption molecule Os(phen)<sub>3</sub><sup>2+</sup> as a photosensitizer in TTA-UC, the  $\eta_{UC}$  was only 5.9% because of its short triplet lifetime ( $\sim 10^2$  ns).<sup>28</sup>

The intramolecular triplet energy transfer (ITET) mechanism was introduced to design a traditional photosensitizer<sup>29,30</sup> and an S-T absorption photosensitizer<sup>3,31</sup> with prolonged lifetime via formation of excited-state thermal equilibrium. By

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**Figure 1.** (a) Molecular structure of the photosensitizers and acceptor; (b) absorption spectra (solid line) and the phosphorescence emission spectra (dotted line,  $\lambda_{\text{ex}} = 663$  nm) of  $\text{Os}(\text{phen})_3^{2+}$  and  $\text{Os}(\text{phen})_3^{2+}\text{-Pe}$ . [ $\text{photosensitizer}$ ] =  $1 \times 10^{-5}$  M, 1,2-dichloroethane as the solvent.

directly conjugating  $\text{Os}(\text{phen})_3^{2+}$  with an energy-pooling acceptor 9,10-diphenyl anthracene (DPA), we recently constructed an ITET-featured molecular dyad  $\text{Os}(\text{phen})_3^{2+}\text{-DPA}$  and extended its triplet lifetime to 1.1  $\mu\text{s}$ . The  $\eta_{\text{UC}}$  was thereby boosted to 9.7% with a simultaneously large anti-Stokes shift of 1.12 eV when pairing with 9-phenyl-10-(*p*-tolyl)anthracene in the solution state.<sup>31</sup> However, the sensitizer's lifetime and TTA-UC efficiency were still suboptimal for practical applications because of the occurrence of notorious thermally reverse triplet energy transfer (RTET) from the  ${}^3\text{DPA}^*$  unit to the  $\text{Os}(\text{phen})_3^{2+}$  unit, considering the fact that the energy difference ( $\Delta E_{\text{TT}}$ ) between  $\text{Os}(\text{phen})_3^{2+}$  ( $T_1 = 1.80$  eV) and DPA ( $T_1 = 1.75$  eV) was merely 0.05 eV.

So far, there exist limited examples of efficient TTA-UC systems simultaneously featuring desirable  $\eta_{\text{UC}}$  (>10%) and excitation wavelength above 650 nm. In the solid matrix where the chromophore diffusion is restricted, the performances of deep-red/NIR excitable TTA-UC materials are even worse. In this context, we report herein a new Os(II) dyad denoted as  $\text{Os}(\text{phen})_3^{2+}\text{-Pe}$  (Figure 1a), with enlarged  $\Delta E_{\text{TT}}$  to 0.27 eV by direct conjugation of  $\text{Os}(\text{phen})_3^{2+}$  with perylene ( $T_1 = 1.53$  eV)<sup>32</sup> to circumvent the RTET and furtherly extend the triplet lifetime to 7.0  $\mu\text{s}$ . The photophysical properties were thoroughly investigated by steady-state and transient absorption/emission spectroscopy. When using  $\text{Os}(\text{phen})_3^{2+}\text{-Pe}$  as a triplet photosensitizer for TTA-UC with 9,10-bis-(phenylethynyl)anthracene (BPEA,  $T_1 = 1.26$  eV)<sup>28</sup> as the acceptor, deep-red light (663 nm) was upconverted to bluish green emission (484 nm) in solution with an unprecedented efficiency of 26.3%. Delightfully, the complex also enjoyed high  $\eta_{\text{UC}}$  with a newly designed hydrophilic BPEA derivative bis(4-tetraethylene glycol phenylethynyl)anthracene (BPEA-TEG)<sup>33</sup> in air-saturated hydrogel assembly. These results would greatly propel the application of TTA-UC to many fields.

## RESULTS AND DISCUSSION

### Steady-State Spectra and Theoretical Calculation.

The steady-state absorption and emission spectra of  $\text{Os}(\text{phen})_3^{2+}\text{-Pe}$  and its parent molecule  $\text{Os}(\text{phen})_3^{2+}$  in 1,2-dichloroethane solution are compared in Figure 1b.  $\text{Os}(\text{phen})_3^{2+}$  displayed a direct S-T absorption band at 660 nm ( $\epsilon = 3500$   $\text{cm}^{-1}$   $\text{M}^{-1}$ ) of metal-to-ligand charge transfer ( ${}^3\text{MLCT}$ ) and two intense singlet-singlet absorption peaks at 432 and 481 nm.<sup>28</sup> When being conjugated with perylene, the S-T  ${}^3\text{MLCT}$  absorption band ( $\epsilon = 4000$   $\text{cm}^{-1}$   $\text{M}^{-1}$  at 660 nm) of  $\text{Os}(\text{phen})_3^{2+}\text{-Pe}$  was preserved and nearly overlapped with  $\text{Os}(\text{phen})_3^{2+}$  itself, while only one wide band of singlet-

singlet absorption was centered at 448 nm. This spectral discrepancy with  $\text{Os}(\text{phen})_3^{2+}$  or perylene (Figure S10) hints the strong electronic communication between two subunits of the dyad in the ground state.<sup>32,34</sup> Upon photoexcitation at 663 nm (1.87 eV),  $\text{Os}(\text{phen})_3^{2+}$  displayed an intense phosphorescence emission at 690 nm, and the corresponding excitation energy of the triplet state was determined to be 1.80 eV (Figure 1b, Table 1), reflecting a minimized energy loss (0.07

**Table 1. Photophysical Data of Two Photosensitizers**

compound	$\lambda_{\text{em}}^a$	$T_1/\text{eV}$	$\tau_p/\mu\text{s}$	$\Phi_{\text{ITET}}^c$	$\Phi_{\text{TET}}^d$	$\eta_{\text{UC}}^e$	$\eta_{\text{UC}}^f$
$\text{Os}(\text{phen})_3$	690	1.80	0.36		48	10.1	
$\text{Os}(\text{phen})_3\text{-Pe}$	694	1.49 <sup>b</sup>	7.0	97	88	26.3	7.1

<sup>a</sup>The peak wavelength of phosphorescence emission ( $\lambda_{\text{ex}} = 663$  nm).

<sup>b</sup>DFT calculated values. <sup>c</sup>Intramolecular triplet energy transfer efficiency, %.

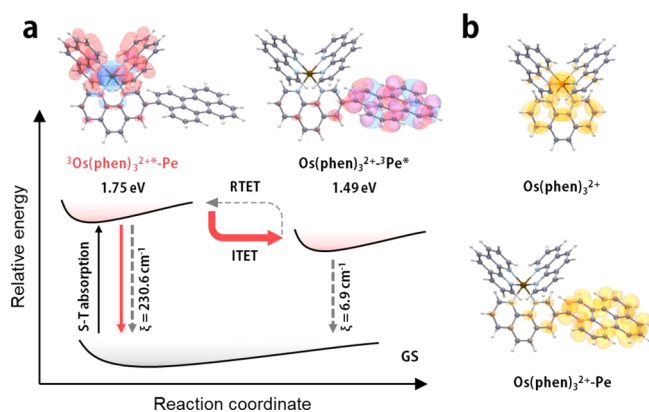
<sup>d</sup>Triplet-triplet energy transfer efficiency with BPEA as the acceptor, %.

<sup>e</sup>TTA-UC emission efficiency with BPEA as acceptor, %, using methylene blue as a standard ( $\Phi_{\text{FL}} = 3\%$  in water).

<sup>f</sup>TTA-UC emission efficiency of the air-saturated hydrogel.

eV) in the intersystem crossing process to form the triplet excited state. A similar phosphorescence position ( $\lambda_{\text{em}} = 694$  nm) and spectral shape were observed for  $\text{Os}(\text{phen})_3^{2+}\text{-Pe}$  too, suggesting the anti-Kasha nature of this emission band with  ${}^3\text{Os}(\text{phen})_3^{2+}\text{-Pe}$  as the emitting species. Meanwhile, the significant reduction of phosphorescence intensity was ascribable to the efficient ITET process from  ${}^3\text{Os}(\text{phen})_3^{2+}\text{-Pe}$  to a stable and dark state  $\text{Os}(\text{phen})_3^{2+}\text{-Pe}^*$ .<sup>22</sup> Based on the quenched phosphorescence intensity, the ITET efficiency ( $\Phi_{\text{ITET}}$ ) was estimated to be  $\sim 97\%$ .

The time-dependent density functional theory (DFT) calculations were performed to predict the locally excited nature for the  $T_1$  of the  $\text{Os}(\text{phen})_3\text{-Pe}$  dyad with the overlapped "hole"/"particle" components in natural transition orbitals at perylene, whereas the  ${}^3\text{MLCT}$  transition from the Os(II) center to two unmodified phenanthroline ligands was more destabilized in energy (Figure 2a). In other words, two kinds of triplet states are formed and correlated to  $\text{Os}(\text{phen})_3^{2+}\text{-Pe}^*$  and  ${}^3\text{Os}(\text{phen})_3^{2+}\text{-Pe}$ , respectively. The effect of weak ground-state electron connection between the  $\text{Os}(\text{phen})_3^{2+}$  unit and Pe unit slightly lowers the  $\text{Os}(\text{phen})_3^{2+}\text{-Pe}^*$  energy level to 1.49 eV in comparison to that of perylene itself, providing a  $\Delta E_{\text{TT}}$  of 0.26 eV to sufficiently suppress the RTET process. Because the Os(II) center has no contribution to frontier molecular orbitals of  $\text{Os}(\text{phen})_3^{2+}\text{-Pe}^*$  in the  $T_1$  state, the SOC matrix element of  $\text{Os}(\text{phen})_3^{2+}\text{-Pe}^*$  with the ground state has been determined to be  $\xi = 6.9$   $\text{cm}^{-1}$ ,



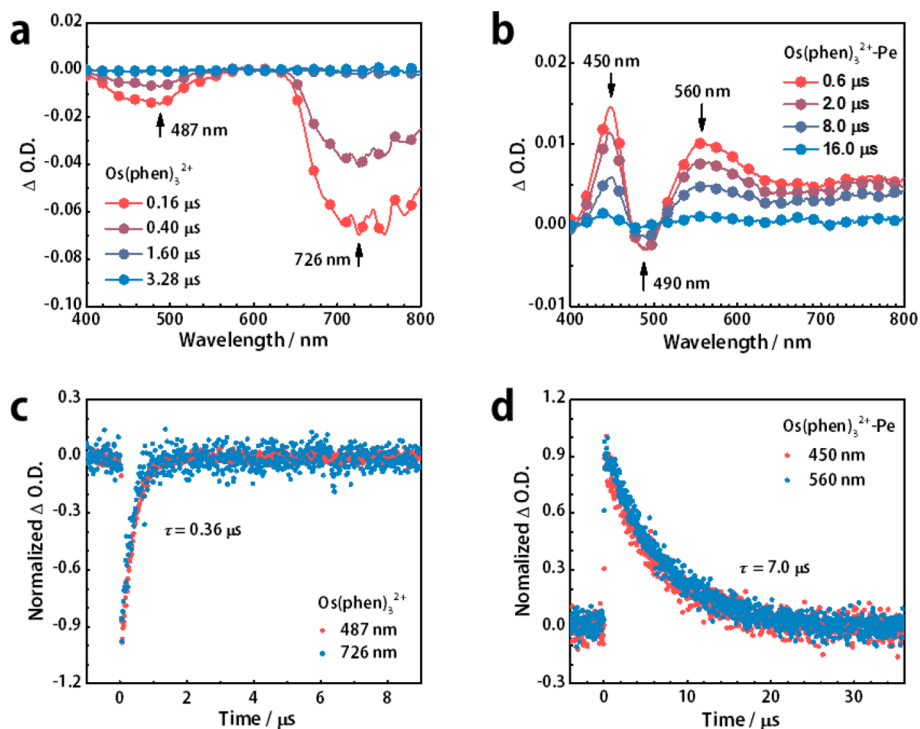
**Figure 2.** (a) Frontier molecular orbitals involved in the low-lying singlet and triplet excited states of the photosensitizers; (b) SDSs at optimized geometries of triplet excited states. Calculations were performed at the B3LYP/6-31G(d) level, and 1,2-dichloroethane was used as the solvent.

which is significantly smaller than that of  ${}^3\text{Os}(\text{phen})_3^{2+*}\text{-Pe}$  ( $\xi = 230.6 \text{ cm}^{-1}$ ), in line with the  ${}^3\text{MLCT}$  nature of the emission band. In the optimized triplet geometry, the spin density surface (SDS) for  $\text{Os}(\text{phen})_3^{2+}\text{-Pe}$  is largely located at a less sterically hindered perylene unit, as shown in Figure 2b, and agrees well with the electronic structure of its lowest triplet state.<sup>35</sup> Comparatively, the SDS mainly resided on the shielded Os(II) atom and one phenanthroline ligand in the parent compound.

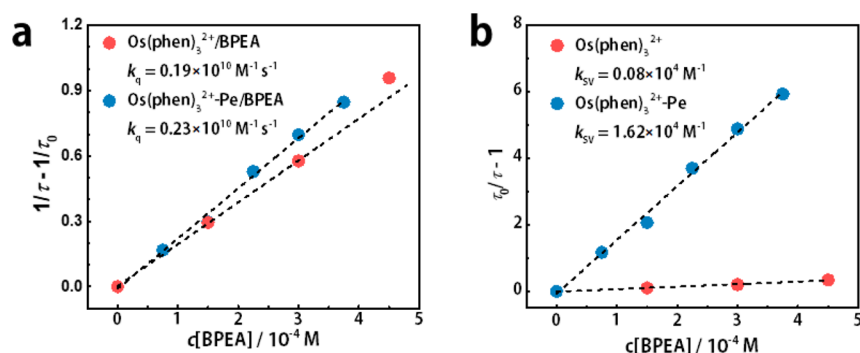
**Triplet Properties and Triplet Energy Transfer Process.** To gain further insight into the triplet excited-state properties of the photosensitizers, nanosecond transient absorption spectra were recorded following photoexcitation at 532 nm. For  $\text{Os}(\text{phen})_3$ , only two negative absorption bands

were observed at 487 and 726 nm (Figure 3a), representing the ground-state bleaching (GSB) peak and the phosphorescence of  $T_1 \rightarrow S_0$ , respectively. The two bands exhibit similar kinetic profiles (Figure 3c) with lifetimes of 0.36  $\mu\text{s}$ , agreeing with their correlation to the  $T_1$  state. For  $\text{Os}(\text{phen})_3^{2+}\text{-Pe}$ , the absorption band from 400 to 600 nm is the superposition of the GSB peak and the triplet–triplet absorption bands of the perylene unit. A weaker GSB band can be still observed at 490 nm that corresponds to the absorption peak of  $\text{Os}(\text{phen})_3^{2+}$  and the perylene unit (Figure 1b), and two intense positive absorption bands at 450 and 560 nm were rationalized to be the triplet–triplet absorption ( $T_1 \rightarrow T_n$ ) bands of perylene unit.<sup>32</sup> Significantly, we did not observe any phosphorescence emission of the  $\text{Os}(\text{Phen})_3^{2+}\text{-Pe}$  segment at 726 nm, indicating that the triplet state is mainly located at the perylene unit because of the highly efficient ITET process. Figure 3d shows decay curves of these positive signals, deducing a nearly 20-fold increase of triplet lifetime ( $\tau_p = 7.0 \mu\text{s}$ ) compared to the parent molecule by single-exponential fitting. It is worth noting that the triplet lifetime of  $\text{Os}(\text{phen})_3^{2+}\text{-Pe}$  is even longer than that of the red light-absorbing benchmark photosensitizers (i.e., Pd(II) octabutoxyphthalocyanine,  $\tau_p = 3.5 \mu\text{s}$ ).<sup>36</sup> These results unambiguously validated the ITET process from the  $\text{Os}(\text{phen})_3^{2+}$  moiety to the adjacent perylene unit upon photoexcitation.

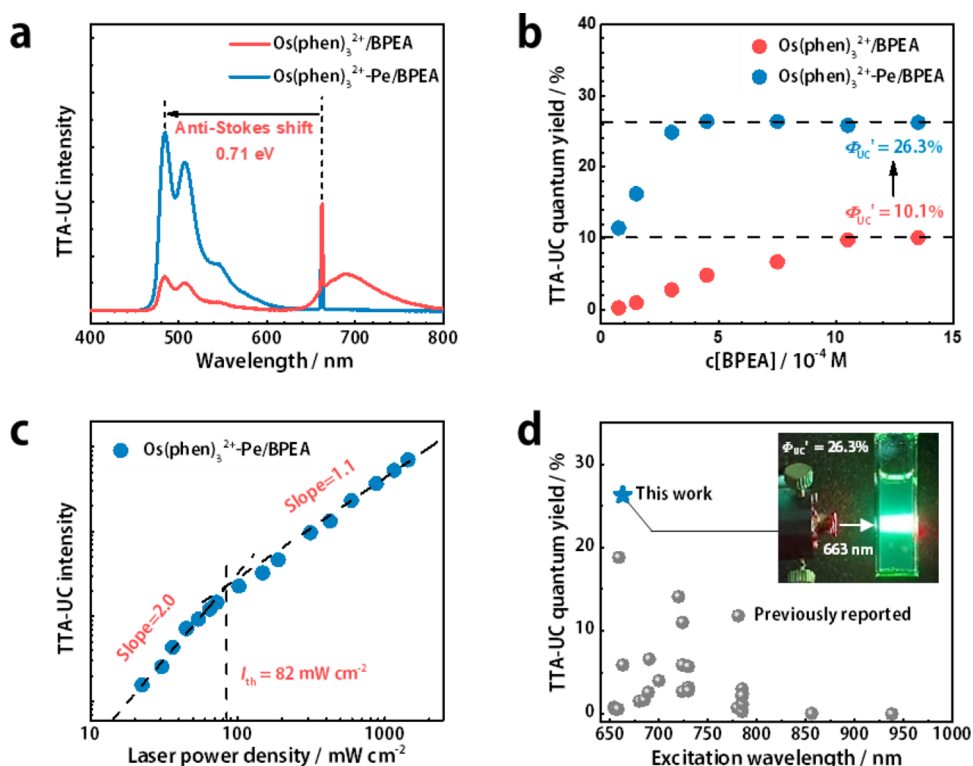
Following the formation of the triplet photosensitizer  $\text{Os}(\text{phen})_3^{2+}\text{-}^3\text{Pe}^*$ , BPEA was selected as the triplet energy acceptor for triplet energy transfer because of suitable exothermicity of the triplet energy gap. The bimolecular quenching rates ( $k_q$ ) and the Stern–Volmer quenching rate constants ( $k_{SV}$ ) were deduced by triplet lifetime changes of photosensitizers in the presence of the acceptor (Figures S12 and S13), according to eqs 1 and 2,



**Figure 3.** (a and b) Nanosecond transient absorption spectra and (c and d) decay kinetic curves of  $\text{Os}(\text{phen})_3^{2+}$  and  $\text{Os}(\text{phen})_3^{2+}\text{-Pe}$ , respectively. [photosensitizer] =  $1 \times 10^{-5} \text{ M}$ , 1,2-dichloroethane as the solvent,  $\lambda_{\text{ex}} = 532 \text{ nm}$ .



**Figure 4.** (a) Bimolecular quenching rates of the triplet photosensitizers; (b) Stern–Volmer plots generated from the triplet excited-state lifetime quenching curves of the compounds measured as a function of BPEA concentration. [photosensitizer] =  $1 \times 10^{-5}$  M, 1,2-dichloroethane as a solvent,  $\lambda_{\text{ex}} = 532$  nm.



**Figure 5.** (a) TTA-UC emission spectra; (b) dependence of the  $\eta_{\text{UC}}$  on acceptor concentration; (c) double logarithmic plot of the TTA-UC fluorescence intensity as a function of excitation power density. [photosensitizer] =  $1 \times 10^{-5}$  M, [BPEA] = 0.4 mM, 1,2-dichloroethane as the solvent, laser excitation wavelength at 663 nm. (d)  $\eta_{\text{UC}}$  values in previously reported TTA-UC systems with the excitation wavelength in the first biological transparency windows (650–900 nm) and this work (see detailed data in Table S1).

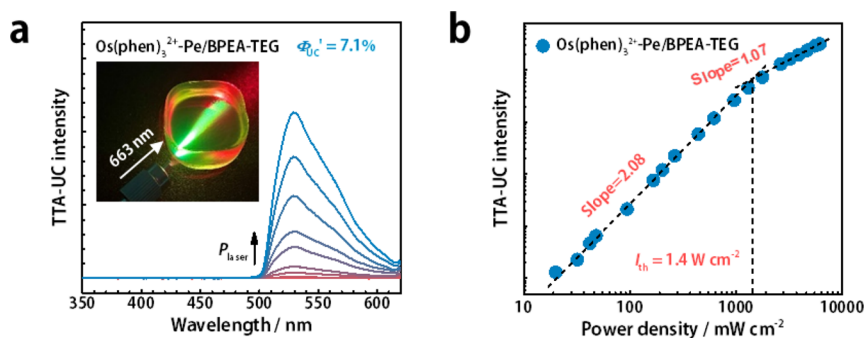
$$1/\tau - 1/\tau_0 = k_q \times [\text{BPEA}] \quad (1)$$

$$\tau_0/\tau - 1 = k_{\text{SV}} \times [\text{BPEA}] \quad (2)$$

where  $\tau_0$  and  $\tau$  represent the triplet lifetime in the absence and presence of BPEA in various concentrations (Table S2), respectively. As shown in Figure 4a, the  $k_q$  value for  $\text{Os}(\text{phen})_3^{2+}\text{-Pe}/\text{BPEA}$  ( $2.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) slightly surpassed that of  $\text{Os}(\text{phen})_3^{2+}/\text{BPEA}$  ( $1.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) but is still much lower than the diffusion rate limit ( $k_{\text{diffuse}} = 8.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C in 1,2-dichloroethane). Such  $k_q$  enhancement from  $\text{Os}(\text{phen})_3^{2+}$  to  $\text{Os}(\text{phen})_3^{2+}\text{-Pe}$  can be likely ascribed to the shielded SDS of  $\text{Os}(\text{phen})_3^{2+}$  as indicated by theoretical results (vide supra), which causes more restricted triplet energy transfer in the  $\text{Os}(\text{phen})_3^{2+}/\text{BPEA}$  system. Meanwhile,  $k_{\text{SV}}$  of  $\text{Os}(\text{phen})_3^{2+}\text{-Pe}$  is determined to be 20-fold larger than

that of the parent compound (Figure 4b,  $k_{\text{SV}} = 1.62 \times 10^4 \text{ M}^{-1}$  for  $\text{Os}(\text{phen})_3^{2+}\text{-Pe}$  and  $k_{\text{SV}} = 0.08 \times 10^4 \text{ M}^{-1}$  for  $\text{Os}(\text{phen})_3^{2+}$ ). This can be readily attributed to the prolonged triplet-state lifetimes of  $\text{Os}(\text{phen})_3^{2+}\text{-Pe}^*$ .

**TTA-UC Property in Solution.** The long-lived excited state and the higher  $k_{\text{SV}}$  value promise  $\text{Os}(\text{phen})_3^{2+}\text{-Pe}$  to be a better triplet photosensitizer for TTA-UC application than  $\text{Os}(\text{phen})_3^{2+}$ . In deoxygenated 1,2-dichloroethane solution, intense greenish upconverted emission from the binary  $\text{Os}(\text{phen})_3^{2+}\text{-Pe}/\text{BPEA}$  system was observed with unaided eyes under photoexcitation at 663 nm (Figure 5d). According to the TTA-UC emission spectra (Figure 5a), the upconverted emission occurred at 484 nm with a substantial anti-Stokes shift of 0.71 eV (the energy difference between the excitation wavelength and the strongest UC emission peak). To



**Figure 6.** (a) TTA-UC emission spectra with increased excitation power density, inset: photograph of TTA-UC fluorescence in hydrogels in an ambient air-saturated atmosphere; (b) double logarithmic plot of the TTA-UC intensity as a function of excitation power density in hydrogels, with a laser excitation wavelength of 663 nm.

maximize  $\eta_{UC}$ , the acceptor usually is in an adequately high concentration to saturate a triplet energy transfer process. Nonetheless, an excessive amount of acceptor might reduce the fluorescence quantum yield because of self-absorption or formation of excimers.<sup>37</sup> It was hence necessary to assess the influence of BPEA concentration on  $\eta_{UC}$  (Figures Sb and S14). For the Os(phen)<sub>3</sub><sup>2+</sup>/BPEA system,  $\eta_{UC}$  increases monotonously with the increased amount of BPEA and culminates at a concentration of ca. 1 mM, and the corresponding maximal  $\eta_{UC}$  value is determined to be 10.1% as well as the triplet energy transfer efficiency ( $\Phi_{TET}$ ) value of 48%. Comparatively,  $\eta_{UC}$  of Os(phen)<sub>3</sub><sup>2+</sup>-Pe/BPEA rapidly reaches a maximum of 26.3% with [BPEA] of only 0.45 mM, while the  $\Phi_{TET}$  value is up to 88% (Table 1). To the best of our knowledge, this is the highest upconversion efficiency reported in the TTA-UC system with photoexcitation in the first biological transparency window (Figure 5d). Such a significant improvement of  $\eta_{UC}$  is associated with the larger collision probability and the higher  $\Phi_{TET}$  because of prolonged triplet lifetime of Os(phen)<sub>3</sub><sup>2+</sup>-Pe.

The TTA-UC fluorescence intensity usually shows a quadratic dependence on excitation power density at low intensities and a linear dependence at high power density, with the intersection of the two extension lines defined as the threshold excitation power density  $I_{th}$ .<sup>38,39</sup> Figure 5c shows a slope change from 2 to 1 in the double logarithmic plot of upconversion emission intensity versus laser power density of the Os(phen)<sub>3</sub><sup>2+</sup>-Pe/BPEA system (Figure S15), where  $I_{th}$  is determined to be 86 mW cm<sup>-2</sup>. The  $I_{th}$  value is apparently lower than that of the Os(phen)<sub>3</sub><sup>2+</sup>/BPEA system (150 mW cm<sup>-2</sup>)<sup>28</sup> and those previously reported data with adopting other S-T absorption photosensitizers (132–320 mW cm<sup>-2</sup>).<sup>27,31</sup> To understand the essential determinants of this low  $I_{th}$  value, we referred to the following equation reported by Monguzzi et al.,<sup>38,40</sup>

$$I_{th} = \frac{(k_A^T)^2}{\epsilon \Phi_{TET} \gamma_{TT}} \quad (3)$$

where  $k_A^T$  is the triplet decay rate of the acceptor,  $\epsilon$  is the molar extinction coefficient of the photosensitizer at excitation wavelength, and  $\gamma_{TT}$  is the second-order annihilation constant for the TTA process. Because Os(phen)<sub>3</sub><sup>2+</sup>/BPEA and Os(phen)<sub>3</sub><sup>2+</sup>-Pe/BPEA share the almost same  $k_A^T$  and  $\gamma_{TT}$  while these two photosensitizers possess similar  $\epsilon$  values, the larger  $\Phi_{TET}$  of Os(phen)<sub>3</sub><sup>2+</sup>-Pe/BPEA was thereby the main reason for its reduced  $I_{th}$  compared to that of Os(phen)<sub>3</sub><sup>2+</sup>/BPEA. This reciprocal relationship clearly indicates that the

introduction of ITET into the S-T absorption photosensitizers can efficiently enhance the sensitivity of the TTA-UC system to incident light.

**TTA-UC Property in Solids.** For better practicability, photon upconversion in solid materials for potential device integration is highly desirable. Because Kim et al. first reported the green-to-blue TTA-UC in a rubbery copolymer, many groups have realized TTA-UC with various polymeric host matrices including polyurethane,<sup>41,42</sup> polybutylacrylate,<sup>43</sup> molecular glasses,<sup>44</sup> supramolecular organogels,<sup>45,46</sup> polyvinyl alcohol,<sup>46</sup> polyacrylate,<sup>47</sup> poly(olefin sulfone)s,<sup>48</sup> hydrogels,<sup>49,50</sup> and thiol-ene polymers.<sup>51</sup> Among them, it has also been demonstrated that the polymer can be used as a nice and direct participant in TTA-UC systems.<sup>41</sup> However, for deep-red/NIR photosensitizers, the short excited-state lifetimes usually cause insufficient triplet energy transfer in such diffusion-restricted media, while the present investigation provides a viable strategy to circumvent this obstacle. With the aim to fabricate an oxygen-tolerant deep-red-absorbing TTA-UC soft material, we followed the protocol from Kimizuka and co-workers by embedding the TTA-UC pair Os(phen)<sub>3</sub><sup>2+</sup>-Pe and BPEA-TEG in a hydrogel composed of gelatin and Triton X-100.<sup>49</sup> The acceptor was functionalized with oligoethylene glycol chains to enhance its hydrophilicity with marginal impact on its photophysical properties. Under ambient conditions, the hydrogel emits naked-eye observable green emission upon photoexcitation at 663 nm in the air-saturated state (Figure 6a). The TTA-UC emission peak at 527 nm is similar to the inherent fluorescence of BPEA-TEG (Figure S11), indicating that the triplet energy transfer process to the acceptor is operable even in a viscous matrix. The  $\eta_{UC}$  is subsequently determined to be 7.1% in hydrogel media, while the  $I_{th}$  value is 1.4 W cm<sup>-2</sup> (Figure 6b). In comparison to the reported TTA-UC hydrogels,<sup>49,50</sup> the  $I_{th}$  of the Os(phen)<sub>3</sub><sup>2+</sup>-Pe/BPEA-TEG system is relatively large, likely ascribing to the moderate molar extinction coefficient of Os(phen)<sub>3</sub><sup>2+</sup>-Pe and the poor hydrophilicity limits the movement of BPEA-TEG.

## CONCLUSIONS

In brief, a new Os(II) complex dyad simultaneously featuring direct S-T absorption and long triplet lifetime has been constructed and utilized as the triplet photosensitizer for deep-red-to-blue TTA-UC. The ITET from the Os(phen)<sub>3</sub><sup>2+</sup> segment to the perylene unit in Os(phen)<sub>3</sub><sup>2+</sup>-Pe highly efficiently occurs ( $\Phi_{ITET} = 97\%$ ), as validated by nanosecond transient absorption and steady-state fluorescence spectroscopy. Compared to unfunctionalized Os(phen)<sub>3</sub><sup>2+</sup> ( $\tau_p = 0.36 \mu s$ ),

the new dyad exhibits a nearly 20-fold increase of triplet lifetime ( $\tau_p = 7.0 \mu\text{s}$ ) because of a suitable triplet energy difference between two subunits. As a result, a much higher triplet energy transfer efficiency is obtained when pairing with BPEA as the energetically suitable acceptor. The bimolecular quenching rate of  $\text{Os}(\text{phen})_3^{2+}\text{-Pe/BPEA}$  is also superior to that of  $\text{Os}(\text{phen})_3^{2+}\text{/BPEA}$  because of the larger collision probability. Consequently,  $\text{Os}(\text{phen})_3^{2+}\text{-Pe/BPEA}$  displays a record-breaking TTA-UC emission efficiency ( $\eta_{\text{UC}} = 26.3\%$ ) for the photoexcitation in the first biological transparency windows of the TTA-UC system, with a large anti-Stokes shift as high as 0.71 eV in deaerated solution. Moreover, the ITET-featured photosensitizer also promises a bright upconverted emission with  $\eta_{\text{UC}} = 7.1\%$  in an air-saturated hydrogel. This work offers a viable strategy to promote upconversion efficiency and will greatly propel real applications of TTA-UC in bioimaging and photovoltaics.

## EXPERIMENTAL SECTION

**TTA-UC Emission Efficiency.** The absorption spectra of the standard in diluted solutions were recorded to obtain the absorbance at excitation wavelength less than 0.05. The quantum yield of the sample could be determined by integrating the emission band of the standard and sample.<sup>52</sup> Using methylene blue as the standard in the present experiments, the  $\eta_{\text{UC}}$  was calculated using eq 4,

$$\eta_{\text{UC}} = 2\Phi_{\text{std}} \cdot \left( \frac{A_{\text{std}}}{I_{\text{std}}} \right) \cdot \left( \frac{I_{\text{sam}}}{A_{\text{sam}}} \right) \cdot \left( \frac{n_{\text{sam}}}{n_{\text{std}}} \right)^2 \quad (4)$$

where  $A$ ,  $I$ , and  $n$  are the absorbance, the integrated emission spectra, and the refractive index of solvents, and 'std' and 'sam' are the standard and samples, respectively. To normalize the maximum  $\eta_{\text{UC}}$  to be unity, eq 1 was multiplied by a factor of 2.

**ITET Efficiency.** The calculation method was based on the quenching of fluorescence or phosphorescence intensity by intramolecular energy transfer. The ITET efficiency ( $\Phi_{\text{ITET}}$ ) was calculated using eq 5,

$$\Phi_{\text{ITET}} = \frac{\Phi_{\text{D-A}}}{\Phi_{\text{D}}} \quad (5)$$

where  $\Phi_{\text{D-A}}$  is the fluorescence (phosphorescence) quantum yield of the dyad;  $\Phi_{\text{D}}$  is the fluorescence (phosphorescence) quantum yield of the energy donor.

**Preparation of TTA-UC Hydrogels.** The preparation method of the hydrogel was according to a previous protocol.<sup>49</sup> In particular, to a mixture of 0.1 mM  $\text{Os}(\text{phen})_3^{2+}\text{-Pe}$  and 20 mM BPEA-TEG in 0.1 mL TX-100 was added 1 mL of 20 wt % hot gelatin solution (80 °C). The mixture was stirred at 90 °C until the suspension transformed into homogeneous solution. This solution was kept at room temperature overnight to obtain the TTA-UC hydrogel.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c02846>.

Commercial instruments, nanosecond time-resolved transient absorption spectra, TTA-UC spectra, nuclear magnetic resonance spectra, high-resolution mass spectra, and the decay curves (PDF)

## AUTHOR INFORMATION

### Corresponding Authors

Xiaosong Cao – Shenzhen Key Laboratory of Special Functional Materials, Guangdong Research Center for Interfacial Engineering of Functional Materials, College of

Materials Science and Engineering, Shenzhen University, Shenzhen 518060, China; Email: [xcao@szu.edu.cn](mailto:xcao@szu.edu.cn)

Xiaoguo Zhou – Department of Chemical Physics, University of Science and Technology of China, Hefei, Anhui 230026, China; [orcid.org/0000-0002-0264-0146](https://orcid.org/0000-0002-0264-0146);

Email: [xzhou@ustc.edu.cn](mailto:xzhou@ustc.edu.cn)

Chuluo Yang – Shenzhen Key Laboratory of Special Functional Materials, Guangdong Research Center for Interfacial Engineering of Functional Materials, College of Materials Science and Engineering, Shenzhen University, Shenzhen 518060, China; [orcid.org/0000-0001-9337-3460](https://orcid.org/0000-0001-9337-3460); Email: [clyang@szu.edu.cn](mailto:clyang@szu.edu.cn)

## Authors

Yaxiong Wei – Shenzhen Key Laboratory of Special Functional Materials, Guangdong Research Center for Interfacial Engineering of Functional Materials, College of Materials Science and Engineering, Shenzhen University, Shenzhen 518060, China; School of Physics and Electronic Information, Anhui Normal University, Wuhu, Anhui 241000, China

Yuanming Li – Department of Chemical Physics, University of Science and Technology of China, Hefei, Anhui 230026, China

Zefeng Li – Shenzhen Key Laboratory of Special Functional Materials, Guangdong Research Center for Interfacial Engineering of Functional Materials, College of Materials Science and Engineering, Shenzhen University, Shenzhen 518060, China

Xinsheng Xu – School of Physics and Electronic Information, Anhui Normal University, Wuhu, Anhui 241000, China

Complete contact information is available at:

<https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c02846>

## Author Contributions

Y.W. synthesized the organic photosensitizer, measured the spectra, performed theoretical calculation, and prepared the first version of the manuscript. Y.L. and Z.L. assisted in the synthesis of photosensitizer molecules and spectral measurements. X.X. assisted in spectral measurements. C.Y., X.Z., and X.C. conceived the idea and led the project. All authors contributed to the final version.

## Notes

The authors declare no competing financial interest.

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