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Highly Effective Near-Infrared Activating Triplet—Triplet Annihilation Upconversion for Photoredox Catalysis

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ABSTRACT: Organic triplet-triplet annihilation upconversion (TTA-UC) materials have considerable promise in areas as broad as biology, solar energy harvesting, and photocatalysis. However, the development of highly efficient near-infrared (NIR) light activatable TTA-UC systems remains extremely challenging. In this work, we report on a method of systematically tailoring an annihilator to attain such outstanding systems. By chemical modifications of a commonly used perylene annihilator, we constructed a family of perylene derivatives that have simultaneously tailored triplet excited state energy (T₁) and singlet excited state energy (S₁), two key annihilator factors to determine TTA-UC performance. *Via* this method, we were able to tune the TTA-UC system from an endothermic type to an exothermic one, thus



significantly elevating the upconversion performance of NIR light activatable TTA upconversion systems. In conjunction with the photosensitizer PdTNP (10 μ M), the upconversion efficiency using the optimal annihilator (100 μ M) identified in this study was measured to be 14.1% under the low-power density of NIR light (100 mW/cm², 720 nm). Furthermore, using such a low concentration of perylene derivative, we demonstrated that the optimal TTA-UC pair developed in our study can act as a highly effective light wavelength up-shifter to enable NIR light to drive a photoredox catalysis that otherwise requires visible light. We found that such an NIR driven method is highly effective and can even surpass directly visible light driven photoredox catalysis. This method is important for photoredox catalysis as NIR light can penetrate much deeper in colored photoredox catalysis reaction solutions, especially when done in a large-scale manner. Furthermore, this TTA-UC mediated photoredox catalysis reaction is found to be outdoor sunlight operable. Thus, our study provides a solution to enhance NIR activatable organic upconversion and set the stage for a wide array of applications that have previously been limited by the suboptimal efficiency of the existing TTA upconversion materials.

■ INTRODUCTION

Photon upconversion provides the possibility to convert lowenergy near-infrared photons (650-1300 nm) under lowirradiation conditions to high-energy light emission.^{1,2} In particular, materials that can upconvert near-infrared light (NIR) to visible emissions have considerable promise in wideranging applications in solar energy harvesting,³ photocatalysis,⁴ and biology⁵⁻⁷ For example, such upconversion systems are able to enhance the utilization of near-infrared photons from the solar energy spectrum in order to increase the efficiency of solar energy harvesting.⁸⁻¹⁰ Moreover, due to their deep tissue penetration ability, reduced photon damage, and decreased light scattering, NIR absorbing upconversion materials have great potential for the exploration of biological applications. $^{5-7}$ In particular, NIR absorbing lanthanide dope upconversion materials have been reported on in numerous areas, such as photodynamic therapy,⁶ biological imaging,^{11,12} chemical sensing,¹³ and optogenetics.^{14,15} Despite holding such promise, inorganic upconversion materials are susceptible to certain inherent challenges, such as the low absorption of

lanthanide ions, concomitant suboptimal upconversion efficiency, and typically require laser light with a relatively high excitation power intensity.^{16,17}

To overcome these key and urgent challenges, organic triplet-triplet annihilation photon upconversion (TTA-UC) materials have emerged as a highly desirable next generation upconversion system.¹⁸⁻³⁰ Compared to their inorganic counterparts, such an organic-based upconversion system generally requires light with a lower power intensity and offers potentially higher quantum efficiency. In general, TTA-UC consists of a two-part system, including a photosensitizer (Sen) molecule and an annihilator molecule (An). As outlined in

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Figure 1. (a) Schematic illustration of the design for our NIR exciting TTA-UC system *via* the optimization of triplet excited state of an annihilator (Py0–Py5). (b) Molecular structures of the photosensitizer (PdTNP) and the group of annihilators (Py0, Py1, Py2, Py3, Py4, and Py5) in this study. (c) Upper: the general rules of design annihilators in TTA-UC. Bottom: the singlet excited state and triplet excited state of PdTNP and the annihilators of Py0–Py5, and the respective TTA-UC efficiencies, 100 mW/cm² under 653 nm laser or 720 nm LED. (d) Photographs of TTA-UC with Py0–Py5 as annihilators, respectively, taken under 100 mW/cm² of 653 nm light.

Figure 1a, in a typical TTA-UC process, the photosensitizer is first excited to its singlet excited state ¹[Sen]* by long wavelength low-energy photons; this is followed by an intersystem crossing (ISC) in order to reach its triplet state ³[Sen]*. The photosensitizer subsequently transfers its triplet excited energy to the triplet excited state of the annihilator ³[An]* through triplet-triplet energy transfer (TTET). Afterward, when the collision of the annihilators in the triplet state occurs, an annihilator can reach an excited-singlet state (1 [An]*), which ultimately leads to an upconverted photon outcome when the annihilator decays back to the ground state.^{18–30}

Despite advances in short wavelength visible light activatable TTA-UC systems, $^{31-34}$ the development of an effective NIR

light activated TTA-UC has been challenging.^{4,35-49} The current NIR light activated TTA-UC typically relied on the photosensitizer optimization, and the respective systems are summarized in Table S1.^{4,35-49} For example, PtTPTNP (TPTNP = tetraphenyltetranaphtho [2,3] porphyrin) wascoupled with rubrene or perylenediimide (PDI) to upconvert 690 nm incident photons into yellow fluorescence. The TTA-UC efficiency of these TTA-UC pairs have been modest, and the TTA-UC efficiency of PtTPTNP/rubrene and PtTPTNP/ PDI have been reported to be 6.6 \pm 0.4% and 6.0 \pm 0.5%, respectively.³⁶ In addition, the photosensitizers of supramolecular ruthenium complexes presented the NIR absorption at 750 nm but their TTA upconversion efficiency was also found to be extremely poor (0.75%) with the annihilator PDI in degassed 2-methyltetrahydrofuran.³⁷ Moreover, a rather low (0.43%) TTA-UC efficiency was observed in solid state film where a lipophilic NIR absorbing osmium complex was used as the sensitizer and rubrene was used as the annihilator.³⁸ The value of this TTA-UC pair in dichloromethane is 0.0047% and in terms of its quantum yield it is 0.00235%. For other osmium complex systems, the TTA-UC efficiencies were also recorded to be modest: 2.7% for the $Os(bptpy)_2^{2+}$ sensitizer and 2,5,8,11-tetra-tert-butylperylene (TTBP) annihilator³⁹ and 5.9% in the pair of $Os(peptpy)_2^{2+}$ and TTBP. The latter of TTA-UC pair-based hydrogel was explored in regard to in vitro optogenetic genome engineering in hippocampal neuron cell culture.40

Moreover, recently, the silyl-substituted anthracene violet annihilator that was coupled with a NIR absorbing osmium complex presented a high TTA-UC efficiency (11%) and large anti-Stokes shift (1.28 eV).⁴¹ The TTA-UC efficiency of NIR absorbing phthalocyanine (e.g., palladium phthalocyanine) photosensitizer together with the diketopyrrolopyrrole derivatives annihilator was 3.2% in degassed toluene.⁴² Meanwhile, under NIR light irradiation, the TTA-UC efficiency (11.2%) was observed in the presence of Pd-phthalocyanine and rubrene.⁴³ In another example, in regard to the TTA-UC pair of Pt(II) meso-tetraphenyltetrabenzoporphine (PtTPBP) sensitizer and 9,10-bis[((triisopropyl)silyl)ethynyl]anthracene (TIPS-Ac) annihilator, direct NIR light excitation at 785 nm (the S_0 to T_1 transition of PtTPBP) led to 2.1% TTA-UC efficiency.⁴⁴ Nevertheless, these above important progresses typically require high annihilator concentrations (>1.0 mM) and relatively high power excitation light density.

On the other hand, visible light driven photoredox catalysis has been used in the synthesis of small molecules, polymers as well as organic nanomaterials.^{50–53} However, there are a series of intrinsic limitations for the use of such visible light illumination in photoredox catalysis, especially for large-scale setup.⁴ More specifically, both the substrates and photocatalysts typically strongly absorb visible light. Thus, substrates compete with photocatalysts for the absorption of incident visible light, leading to suboptimal reaction efficiency. Moreover, the penetration depth of visible light is very shallow through the colored reaction solution, leading to challenges in large-scale reactions. In contrast, due to minimal overlap with the absorption of substrates and photocatalysts, NIR light (>700 nm) has a much deeper penetration depth in these colored reaction mediums.^{4,54,55} However, directly using the low energy of NIR light has been challenging for driving photoredox catalysis.^{56–58} In this regard, TTA-UC has held great promise as the phototransducer to drive photoredox catalysis under NIR light illumination.4,59,60 Yet, such promise has been restricted by the suboptimal NIR activated TTA-UC efficiency. To date, TTA-UC dye pairs that contain the perylene annihilator and platinum(II) tetraphenyltetranaphthoporphyrin (PtTNP) as the sensitizer as well as a TTA-UC pair of furanyldiketopyrrolopyrrole (FDPP) annihilator and palladium(II) octabutoxyphthalocyanine (PdPc) sensitizer have been attempted.⁴ Nevertheless, the TTET process from PtTNP to perylene is an unfavorable endothermic process, as the T_1 state of perylene $(1.53 \text{ eV})^{61}$ is higher laying than the T_1 state of PtTNP (1.39 eV).³⁶ As a consequence, the TTA-UC efficiency was low, at just 2%, even with high concentrations of annihilators perylene (31.3 mM) in conjunction with photosensitizer PtTNP ($10 \mu M$).⁴ Therefore, the development of highly effective exothermic NIR activated TTA-UC is urgently important in regard to light driven photoredox catalysis.

RESULTS AND DISCUSSION

Compared to the above photosensitizer optimization methods, systematic chemically modification of the annihilators may lead to tunable properties of the S1 and T1 states, as well as subsequent improvement of the NIR light activated TTA upconversion performance. Herein, in this work, we attained highly efficient NIR exciting TTA-UC via optimizing the annihilator. In particular, we systematically synthesized a series of perylene derivative compounds and studied their triplet excited states. By doing so, we are able to tune the TTA-UC pair from the endothermic to the exothermic type, as well as improve the ultimate TTA-UC performance. This molecular structural modification was found to be able to simultaneously tune the two key photophysical properties of the Py annihilators in relation to TTA-UC enhancement (i.e., the singlet excited states (1An*) and the triplet excited states $(^{3}An^{*})$). As illustrated in Figure 1a, both the energy levels of ¹An* and ³An* are essential for effective TTA-UC and there are two general rules for designing TTA-UC annihilators: (1) the annihilator should have a lower laying triplet excited state than that of the triplet excited state of the photosensitizer $({}^{3}[An]^{*} < {}^{3}[Sen]^{*})$, allowing an efficient TTET process to occur from photosensitizer to annihilator; (2) the doubled energy of the triplet excited state of the annihilator should be higher than that of the singlet excited state of the annihilator (2 \times ³[An]* > ¹[An]*), enabling the ultimate effective TTAupconversion to take place. Following these rules, we developed a family of the new Py annihilators by altering the aromatic groups appended to Py (Figure 1b). We found that these respective Py derivatives have simultaneously fine-tuned 3 [An]* and 1 [An]*. In this study, we used a typically used NIR absorbing photosensitizer palladium(II) tetraphenyltetranaphthoporphyrin (PdTNP), which has intense absorption in the NIR region ($\lambda_{ex} = 702$ nm, $\varepsilon = 1.64 \times 10^5$ M⁻¹ cm⁻¹) and a long triplet excited lifetime ($\tau_{\rm T}$ = 65 µs) (Table S2).^{62,63} Accordingly, in conjunction with PdTNP, we found that such an annihilator modification strategy was able to systematically enhance the TTA-UC performance by switching the TTA-UC system from the undesired endothermic type (${}^{3}[An]^{*}$ > 3 [Sen]*) to a favorable exothermic one (3 [An]* < 3 [Sen]*). In addition, since the singlet excited energy ¹[Py]* can be simultaneously tuned along with the chemical modification of Py, the ultimate upconverted emission color was found to be able to be adjusted from 490 to 580 nm. In particular, the highest recorded TTA-UC efficiency (16.7%, 0.1 W/cm², 653

nm laser and 14.1%, 0.1 W/cm², 720 nm LED) was found in our optimal TTA-UC system (Figure 1c). Moreover, as a proof-of-principle, we demonstrated that the highly effective exothermic TTA-UC pair identified in our study enables highly effective NIR driven photocatalysis of the conventional visible light photocatalyst of Eosin Y to occur for both small-scale and large-scale reactions.

In particular, the rich and versatile chemistry of Py makes it possible for the rapid, divergent synthesis of the series of Py annihilators. Herein, via a Sonogashira cross-coupling reaction, a group of new annihilators (Py1, Py2, Py3, Py4, and Py5) with an appended aryl-alkynyl to the Py core were able to be synthesized and characterized (Scheme S1). Due to the large and efficient π -conjugation, the absorption and fluorescence wavelengths were found to be red-shifted. The UV-vis absorption spectra of the annihilators cover a wide range of electromagnetic spectra, from 400 to 550 nm (Figure S2). Moreover, the fluorescence of the annihilators occurs at 470-600 nm (Figure S3), and the respective singlet excited energy of the annihilators (1[An]*) systematically decreases from 2.78, 2.60, 2.57, 2.56, and 2.44 to 2.39 eV (Table S4). The fluorescence quantum yields ($\Phi_{\rm F}$) are determined to be 83%, 70%, 72%, 68%, 74%, and 76% for Pv0, Pv1, Pv2, Pv3, Pv4, and Pv5, respectively (Table S2). In addition, the solvent dependency of the UV-vis absorption and the fluorescence emission spectra of Py0-Py5 were measured. All of the annihilators presented similar UV-vis absorption in solvents of different polarities (toluene, DCM, THF, and DMF), suggesting that the ground state of annihilators is not sensitive for the polarity of solvents (Figure S4).⁶⁴ Moreover, the annihilators have similar fluorescence intensity and profiles in solvents of different polarities, indicating that the S1 state of the annihilators is not affected by solvents' polarity (Figure S5).65

The cyclic voltammograms of annihilators Py0–Py5 were measured (Figures S6–S11 and Table S5). We only observed reversible oxidation with $E_{1/2}$ values of 1.02, 0.99, 0.99, 0.84, 0.94, and 0.98 V vs Ag/AgCl, respectively. Compared to other annihilators, due to the electron-donating carbazole substituted perylene, Py3 presented a lower oxidation potential of 0.84 V.

To better understand the electronic properties of these perylene derivatives Py0–Py5, their ground state geometry was optimized at the B3LYP/6-31+G(d) level of density functional theory (DFT) (Figures S12–S17). Their HOMOs and LUMOs are well-distributed over perylene cores, but only partial electron density is observed for their phenylethynyl moieties. Their energy band gaps were estimated to be 2.87, 2.58, 2.51, 2.52, 2.24, and 2.22 eV for Py0–Py5, respectively, which is consistent with the results from the experiments (Table S4).

Next, we studied the T_1 of the annihilators. We estimate the T_1 state of annihilators by the triplet-triplet energy transfer (TTET) method.^{66–68} In the experiment, we selected mesotetraphenyl-tetrabenzoporphine palladium complex (PdTPBP) and PdTNP as photosensitizers, which have different wavelengths of phosphorescence emission. According to phosphorescence spectra of PdTPBP and PdTNP, we calculated the T_1 values as 1.55 and 1.33 eV, respectively. When the annihilators were titrated into the solution of PdTPBP or PdTNP, the phosphorescence were observed to be significantly quenched, indicating that the T_1 of annihilators is lower than the T_1 of the photosensitizers (Figure S18). In particular, we observed that the phosphorescence of PdTPBP was clearly quenched for all of the annihilators, suggesting that the T_1 state of Py0–Py5 is

lower than 1.55 eV (Figures \$19-\$24 and Table \$6). By contrast, Py0 did not quench the phosphorescence of PdTNP (Figure S25), suggesting that the range of the T_1 state for Py0 is from 1.55 to 1.33 eV. We observed that the phosphorescence of PdTNP is quenched within high concentrations of Py1-Py3 (Figures S26–S28), suggesting that the T_1 of Py1–Py3 is close to the T₁ of PdTNP. Compared to other annihilators, Py4 and Py5 effectively quench the phosphorescence of PdTNP (Figures S29 and S30), suggesting that the T_1 states of Py4 and Py5 are lower than 1.33 eV. In order to further quantitatively analyze the T1 of these annihilators of Py4 and Py5, we first measured the phosphorescence of Py4 and Py5 at 77 K to determine the T₁ states of Py4 and Py5. However, we still did not observe the phosphorescence emissions of Py4 and Py5 (Figure S31). Therefore, we performed time-dependent density functional theory (TD-DFT) calculations. As can be seen in Table S3, we found that, when the Py core was appended by aryl-alkynyl, the T1 state was calculated to steadily decrease. In particular, the triplet excited state of Py0 is 1.53 eV. This value drops to 1.38 eV for the monoaryl-alkynyl Pys (Py1, Py2, and Py3) and further decreases to 1.23 eV for the diaryl-alkynyl Pys (Py4 and Py5). The results of these calculations are consistent with our estimated T₁ state of Py0-Pv5 via the TTET method. Moreover, the doubled triplet excited energy of Py $(2 \times {}^{3}[An]^{*})$ is higher than the singlet excited state energy (1[An]*) in all of the Py derivatives (Py0, Py1, Py2, Py3, Py4, and Py5) (Table S4), indicating that these perylene derivatives satisfied the condition of being effective annihilators.

For TTA-UC to be efficient, 3 [Sen]* is required to be above 3 [An]*. Thus, favorable exothermic TTA-UC can take place. The triplet excited state of our photosensitizer PdTNP is characterized to be located at 1.33 eV (Figure S1). This energy level is lower than the triplet excited state of the original core perylene molecule (Py0), similar to those of monoaryl-alkynyl Pys (Py1, Py2, and Py3) but surpassed those of diaryl-alkynyl Pys (Py4 and Py5). Thus, accordingly, we anticipated that we can tailor the TTA-UC system from the undesired endothermic type to a favorable exothermic one. As such, the upconversion performance would be divided into three distinctive levels (Py4, Py5 > Py1, Py2, Py3 > Py0).

In order to validate this hypothesis, we conducted experiments to examine the TTA-upconversion properties of this family of Py annihilators in conjunction with the photosensitizer PdTNP. In our study, we found that a high concentration of perylene derivatives will significantly quench the fluorescence intensity of annihilators via inner filter effects (Figures S32-S37).⁶⁹ In addition, the two crucial steps in TTA upconversion, including TTET and TTA, are highly dependent on the concentration of the annihilators.⁷ Therefore, we further explored the optimal concentration of the annihilators in TTA-UC. We found that, by increasing the concentration of annihilators, the TTA-UC first gradually increases. Then, when the concentration of the annihilators exceeds the optimal concentration, the intensity of TTA-UC did not further increase (Figures S38-S42). By doing so, we determined that the optimized concentrations of the annihilators (Py1, Py2, Py3, Py4, and Py5) were to be 600, 1000, 1000, 300, and 100 μ M in the presence of PdTNP (10 μ M), respectively.

Our experimental results agree quite well with our hypothesis. Under the optimal conditions, Py0 was not observed to produce TTA-UC; the monoaryl-alkynyl annihi-



Figure 2. (a) Normalized upconversion emission spectra of Py1–Py5 in toluene, $\lambda_{ex} = 653$ nm (100 mW/cm²). (b) CIE diagram representing the adjustable upconversion emission colors. (c) Upconversion pictures of Py0–Py5 with PdTNP. For Py0–Py3 with PdTNP, the excitation power is 1.0 W/cm²; for Py4 and Py5 with PdTNP, the excitation power is 0.1 W/cm², $\lambda_{ex} = 653$ nm. (d) Threshold intensity and upconversion efficiency of Py1–Py5 in conjunction with PdTNP. (e) Upconversion emission spectra of the TTA-UC system (Py5 (100 μ M) as the annihilator and PdTNP (10 μ M) as the photosensitizer) under argon with various excitation intensities ($\lambda_{ex} = 653$ nm; 5.8, 7.5, 9.4, 15.8, 27.4, 51.3, 60.8, 77.3, 105.9, 146.5, 178.3, 216.6, 263.7, 293, 388.5, 454.8, 532.5, and 636.9 mW/cm²). (f) Dependence of the TTA-UC intensity of the solution of PdTNP and Py5 on the various incident power densities. The results fit the lines that have slopes of 2.06 (black, below) and 1.24 (red, above) in the low- and high-power regions, respectively; I_{th} is 40.7 mW/cm².

lators (Py1, Py2, and Py3) showed modest TTA upconversion signals. In stark contrast, the diaryl-alkynyl annihilators (Py4 and Py5) show intense TTA upconversion emissions (Figure 2c). Moreover, since the systematic chemical modification of Py also shifted the singlet excited state energy of the annihilators, the respective TTA-UC emission colors were found to be able to be simultaneously tuned from 490 to 580 nm. The monoaryl-alkynyl perylene as annihilators (Py1, Py2, and Py3) show that the upconversion luminescences are cyan (Py1) and green (Py2 and Py3). Along with the increase in π conjugation, the TTA-UC emission peaks of Py4 and Py5 further red-shifted and showed yellow and orange colors, respectively (Figure 2c). We calculated their color coordinates in the CIE diagram, which are (0.24, 0.64), (0.30, 0.66), (0.27, 0.67), (0.42, 0.57), and (0.47, 0.53) for Py1, Py2, Py3, Py4, and Py5, respectively (Figure 2b). Moreover, an important parameter for upconversion systems is the excitation rate threshold $(I_{\rm th})$, wherein the upconverted light intensity switches from a quadratic to a linear dependence on incident power. We find that, for Py1, Py2, and Py3, these thresholds are 347.0, 65.3, and 53.7 mW/cm², respectively (Figures S43-S45). For Py4 (Figure S46) and Py5 (Figure 2e,f), the thresholds fall at 42.9 and 40.7 mW/cm², respectively.

The respective upconversion efficiencies were first evaluated under 100 mW/cm² and 653 nm light excitation (Figure S47 and Table S9). In this study, the fluorescence quantum yield of zinc phthalocyanine (ZnPc) in DMF was used as the reference, as this is an established standard method for TTA-UC efficiency measurement. More specifically, TTA-UC emissions for monoaryl-alkynyl appended Pys (Py1, Py2, and Py3) have peaks at 518, 526, and 525 nm, respectively, and their upconversion efficiencies were detected to be 0.062%, 0.25%, and 0.24% in toluene. The TTA-UC efficiencies of diaryl-alkynyl appended Py annihilators (Py4 and Py5) were also measured. When Py4 was used as the annihilator, green emissions peaking at 550 nm were observed and the upconversion efficiency went up to 7.6%. When the Py5 was used as the annihilator, the record highest TTA upconversion efficiency (16.7%) was found.

We then studied the TTA-UC performance of the optimal Py annihilators (Py4 and Py5) under the illumination of 720 nm NIR LED. The transition threshold ($I_{\rm th}$) between the quadratic and the linear regime, respectively, occurs near 46.4 and 46.0 mW/cm² (Figure 3b,e), which is comparable to the value under 653 nm light (Figure 2d). As shown in Figure 3c,f, the upconversion efficiencies of Py4 and Py5 increased and reached a plateau level at 6.4% and 14.1% beyond their respective $I_{\rm th}$ values (46.4 and 46.0 mW cm⁻²) using indocyanine green (ICG, $\Phi_f = 12\%$ in DMSO) as a reference (Table S11). These upconversion efficiencies are similar when we used the calculated $\Phi_{\rm UC}$ (653 nm) to estimate the $\Phi_{\rm UC}$ (720 nm) (Table S10). In addition, the anti-Stokes shifts of PdTNP/Py4 and PdTNP/Py5 are 0.66 and 0.45 eV, respectively. More importantly, such upconversion lumines-



Figure 3. (a) Full UC spectra profile of Py4 as annihilators and PdTNP as photosensitizers under Ar with various excitation intensities at 720 nm $(7.5-160 \text{ mW/cm}^2)$. A 690 nm long-pass filter was used to block potential shorter wavelength light interference from the LED. (b) Dependence of the TTA-UC intensity of the solution of PdTNP and Py4 on the various incident power densities. The results fit the lines that have slopes of 2.02 (black, below) and 0.98 (red, above) in the low- and high-power regions, respectively; the I_{th} is 46.4 mW/cm². (c) Upconversion efficiency of the mixture of PdTNP and Py4 measured as a function of 720 nm incident power density; inset photographs are TTA-UC emission for Py4 under 720 nm LED irradiation (10, 20, and 30 mW/cm²). (d) Full UC spectra profile of Py5 as annihilators and PdTNP as photosensitizers under Ar with various excitation intensities ($\lambda_{ex} = 720 \text{ nm}, 7.5-160 \text{ mW/cm}^2$). A 690 nm long-pass filter was used to block potential shorter wavelength light interference from the LED. (e) Dependence of the TTA-UC intensity of the solution of PdTNP and Py5 on the various incident power densities. The results fit the lines that have slopes of 1.96 (black, below) and 1.07 (red, above) in the low- and high-power regions, respectively; the I_{th} is 46.0 mW/cm². (f) Upconversion efficiency of the mixture of PdTNP and Py5 measured as a function of 720 nm incident power densities.

cence that uses Py4 and Py5 as annihilators is strong enough to be clearly observed by the naked eye under 720 nm NIR LED, with a power density as low as 10 mW/cm² (Figure 3c,f).

In order to explore the reasons for the outcome of the $\Phi_{\rm UC}$ for the different TTA-UC pairs, we measured the phosphorescence quenching within different annihilators and then calculated the Stern–Volmer quenching constant (k_{sv}) and the bimolecular quenching constant (k_q) (Table S7).^{71–73} Py4 and Py5 presented higher k_{sv} values than those of Py1-Py3, indicating that a lower level of the T₁ state of annihilators than PdTNP is beneficial for TTA upconversion. Moreover, we calculated the TTET (Φ_{TTET}) and normalized TTA efficiency (η_{TTA}) of TTA-UC pairs according to a well-established method in the literature (Table S8).^{74–76} Due to the higher T₁ state, the $\Phi_{\rm TTET}$ is as low as 1.87% for Py0. For the Py1–Py3, the Φ_{TTET} values are 5.54%, 17.1%, and 5.97% due to the small energy gap between PdTNP and annihilators, respectively (Figure S48). In contrast, the higher Φ_{TTET} values for Py4 (33.7%) and Py5 (41.1%) were observed in the presence of PdTNP. Additionally, only Py4 and Py5 show high η_{TTA} values, those of 30.4% and 53.2%, respectively. We further explored the microscopic structures of our systems. In particular, we conducted transmission electron microscope (TEM) imaging for the drop-casted PdTNP/Py4 and PdTNP/Py5, and these samples were negatively stained via 5% sodium phosphotungstate (Figure S54). Interestingly, in the TEM imaging, we observed that the more effective UC pair (PdTNP/Py5) can form nanoparticles. This self-assembly is also likely to contribute to the promotion of the TTET process, thereby improving the ultimate TTA-UC efficiency.

Upon identifying the best performing TTA-UC pairs, as a proof-of-principle, we used such TTA-UC pairs as phototransducers in order to study NIR light driven photoredox catalysis in conjunction with conventionally green absorbing photocatalyst of Eosin Y. Photoredox catalysis is a typically complex photochemical process.⁵⁰⁻⁵³ The product yield is dependent on a series of factors, including the intensity of the incident light, the reaction device setup, and the specific nature of the reactions.^{50–53} Although in previous studies NIRactivated photoredox catalysis has been observed with high yields,⁴ the specific power density and the relationship between TTA-UC efficiency and the outcome reaction yields appears to be absent. In addition, in view of the specific nature of different photoredox catalytic reactions, the relationship between the photoredox process and TTA-UC may vary and needs to be investigated on a case-by-case basis. In our work, we chose the photooxidation of aryl boronic acid to phenol as an example of a reaction. Due to mild reaction conditions, high product of yield and good selectivity, such synthesis of the phenols from boronic acids, is much more plausible as compared to the



Figure 4. NIR light activation photooxidation arylphenylboronic acid. (a) Different TTA-UC pairs coupling with Eosin Y mediated photooxidiation under NIR light illumination. (b) Product yields under different reaction volumes; the diameter of the reactor is 3.9 cm, the diameter of the NIR LED beam is 3.1 cm, the rate of magnetic stirring is 300 rpm. (c) Other arylphenylboronic acid photooxidation results.

conventional transformations using aryl halides and aryl diazonium salts as substrates. $^{77-79}$ The PdTNP/Py5 as the brightest TTA-UC pair was found to be effective in conjunction with Eosin Y and the oxidant of $PhI(OAc)_2$ (Figures S49 and S50) for such a NIR light driven reaction. In contrast, we did not observe good product yields for other suboptimal TTA-UC pairs (Py0-Py4 and PdTNP) (Figure 4a). This result not only clearly shows that an increase in the TTA-UC efficiency can lead to improved reaction yields but also suggests that enhancement of TTA-UC efficiency via the rational design of the annihilators is essential to increasing the product yield. Moreover, it is exciting that we further found that such a NIR driven method can even surpass directly visible light driven photoredox catalysis. This is the case because of the reduced photobleaching for the Eosin Y with NIR light. For example, in the absence of the TTA-UC pair, the photocatalytic reaction with green light (530 nm, 20 mW/ cm²) leads to a 76% product yield. (Figure S49, entry 1). In contrast, the combination of the pair of PdTNP and Py5 is able to effectively improve the product yield to 78.2% under an NIR LED (20 mW/cm², 720 nm) (Figure S49, entry 10). Meanwhile, due to the deep penetration of the colored reaction solution for NIR light, we were able to carry out photooxidation in a large-scale reaction. More specifically, for directly visible light driven photooxidation, when we increased the reaction volume from 2 to 20 mL, the product yield significantly dropped from 76% to 28%. In contrast, we

observed a quite insignificant decrease from 78.2% to 60% in the yield of the photooxidation product in the presence of TTA-UC under NIR light (Figure 4b and Figure S51). In addition, we found similar high product yields with a series of other electron-rich, electron-deficient, and electron-neutral arylboronic acids with such a TTA-UC pair (Figure 4c). Interestingly, since only low-power NIR light can activate PdTNP/Py5 to produce bright visible upconversion light, we explored whether outdoor sunlight can drive the photooxidation of aryl boronic acid in order to generate aryl phenol. As a result, in the presence of a 690 nm long pass filter, which can minimize the interference of the shorter wavelength light, the product yield was observed to be 21% in the presence of PdTNP/Py5 and Eosin Y. In contrast, in our control experiment, in the absence of PdTNP/Py5, the product yield of Eosin Y alone was only $\sim 10\%$ (Figure S52). Compared to our results with the Eosin Y alone in the dark (5.4%), the difference is quite insignificant. We would like to note that the sunlight driven reaction yield should be further increased, as our proof-of-concept sunlight reaction setup can be further optimized as well as be done with stirring. These results suggest that, via coupling with a visible light absorbing photocatalyst, the highly effective exothermic NIR activation TTA-UC that we developed as a phototransducer acts as a robust, general photontransducer platform that overcomes the shortcomings of existing visible light driven photoredox catalysis, especially in their large-scale manner. It is also

Finally, we attempted to study the mechanism of photooxidation of aryl boronic acid to produce aryl phenol (Figure S56). In this reaction, the $*[Eosin Y]^1$ is essential for the catalysis of the photooxidation of aryl boronic acid. Under the 653 nm laser, in regard to the Eosin Y only solution, we did not observe the fluorescence emission of Eosin Y at 575 nm, suggesting that a long wavelength light (>650 nm) cannot excite the Eosin Y (Figure S53b). Similarly, under 653 nm light, in the presence of PdTNP/Eosin Y, we did not observe the TTA-UC at 575 nm, indicating that PdTNP is not able to sensitize the Eosin Y to generate the *[Eosin Y] 1 (Figure S53b). In contrast, in the presence of PdTNP/Py5 and Eosin Y, the TTA-UC peaks at 550 and 570 nm were observed to be significantly declined at the same the emission that Eosin Y at 575 nm was found to emerge. This indicates that the ground state of Eosin Y can absorb the TTA-UC from PdTNP/Py5 to produce *[Eosin Y]¹ (Figure S53c). Meanwhile, significant spectra overlap was observed between Py5 emission and Eosin Y absorption, suggesting that the NIR light driven photooxidation of aryl boronic acid is likely to occur via the TTA-UC emission and Eosin Y reabsorption (Figure S53d). Moreover, we compared the product yield in our system under control conditions. As a result, under control conditions, only in the presence of Eosin Y or PdTNP were the product yields very low (7.2% and 4.9%) respectively, under NIR light illumination (Figure S49, entries 3 and 5). Similarly, in the presence of PdTNP/Eosin Y or PdTNP/Pv5, the product yields were also only 5.3% and 5.4%, respectively (Figure S49, entries 6 and 7), which is close to the product yield in the dark (5.7%) (Figure S49, entry 2). In contrast, in our system (PdTNP/Py5 and Eosin Y), the product yield was significantly higher (78.2%). These results further confirmed that both Eosin Y and TTA-UC are essential, as illustrated in our proposed mechanism, where Eosin Y absorbs the TTA-UC from PdTNP/Py5 and is then converted to ¹[Eosin Y] * in order to enable the photooxidation of arylboronic acid.

CONCLUSION

In summary, we have demonstrated that the performance of NIR light mediated TTA upconversion is able to be significantly improved by optimizing the chemical structures of Py annihilators and their respective triplet energy levels. In view of this theory, we obtained the highest recorded NIR to green TTA-UC pair (Φ_{UC} = 16.7% (653 nm) and 14.1% (720 nm), PdTNP and Py5) with a low-concentration annihilator (100 μ M), as well as a low-power density of NIR light. Moreover, via coupling with a visible light absorbing photocatalyst (Eosin Y), we demonstrated that our exothermic NIR activating TTA-UC system can act as an effective phototransducer to boost the photocatalytic yield, especially in large-scale reactions. This system was found to be effective enough to even be operated under ambient sunlight conditions. Together, this study provides a versatile and straightforward approach toward the development of highly efficient TTA-UC pairs that can operate under low-power NIR light. This is particularly valuable for photocatalysts and a variety of biological and solar energy harvesting applications.

ASSOCIATED CONTENT

1 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c06976.

Scheme of synthetic pathways, discussions of chemicals and characterization methods used, measurement of fluorescence quantum yield, electrochemical measurements, calculation of standard oxidation/reduction potential, TTA upconversion characterization, measurement of the upconversion efficiency, Stern-Volmer quenching plot experiment, triplet-triplet energy transfer efficiency measurements, normalized triplet-triplet annihilation efficiency calculation, TEM imaging, visible light and sunlight driven photooxidation arylboronic acid to phenol, and large volume NIR light driven photooxidation aryl boronic acid to phenol, tables of summarized reported NIR to visible light TTA upconversion system, photophysical parameters, DFT calculation for the annihilators, summary of the singlet excited/triplet excited state energy levels, electrochemical properties, Stern-Volmer quenching constant and bimolecular quenching constant, TTET quantum efficiency and normalized TTA efficiency, calculation summary of TTA-UC efficiency, estimated TTA upconversion efficiency, and calculation summary of TTA-UC efficiency, and figures of UV-vis absorption spectra, fluorescence spectra, cyclic voltammograms, electron density maps, simplified Jablonski diagram illustration, phosphorescence intensity decays, Stern-Volmer plots, normalized fluorescence emission spectra, quantitative analysis of the relationship between fluorescence and upconversion intensity and concentration, double-logarithmic plot, TTA-UC spectra, optimization and control experiments, setup of photooxidation of aryl boronic acid to aryl phenol reaction, NIR activated photooxidation of arylboronic acid to arylphenol, reaction setup for the reaction, chemical equations, illustration reaction setups, TEM images, proposed mechanism of NIR driven TTA-UC mediated photooxidation of aryl boronic acid, NMR spectra, and ESI-MS spectra (PDF)

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Notes

The authors declare no competing financial interest.

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