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Photon Upconversion from Near-Infrared to Blue Light with TIPS-Anthracene as An Efficient Triplet-Triplet Annihilator

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ABSTRACT: Photon upconversion (PUC) via triplet-triplet annihilation (TTA) from near-infrared (NIR) to blue photons could have important applications especially to bio-imaging and drug delivery accompanied by photochemical reaction. The fundamental challenges in achieving this has been the large anti-Stokes shift combined with the need to efficiently sensitize within the biological transparency window (700 - 900 nm). This calls for materials combinations with minimal energy losses during sensitization and minimal energy requirements to drive efficient TTA. Here, we demonstrate efficient PUC converting from NIR energy to blue photons using the commercially available material 9,10-Bis[(triisopropylsilyl)ethynyl]anthracene (TIPS-Ac) as the annihilator. With a conventional triplet sensitizing system, TIPS-Ac performed TTA efficiency of $77 \pm 3\%$ despite a relatively small driving force, compared to conventional TTA material converting from NIR to blue, for the TTA of less than 0.32 eV. Combined with Pt(II) meso-Tetraphenyl Tetrabenzoporphine (PtTPBP), which is a heavy atom triplet sensitizer that directly generates triplets upon NIR photon excitation, the resulting system allowed for an anti-Stokes shift of 1.03 eV. Our results highlight the use of direct triplet generation via NIR excitation as a useful path to achieving large anti-Stokes shift and also show that high TTA efficiencies can be achieved even in the absence of large driving energies for the TTA process.

Photon upconversion (PUC) via triplet-triplet annihilation (TTA) is an attractive means for solar energy concentration, bio-imaging, and photochemical reaction, such as photoinduced drug delivery. In particular, generation of blue light (< 500 nm) via upconversion is important, because blue light is required for most photochemical reactions^{1,2}, as well as photocatalytic water splitting to produce hydrogen, since most materials with the efficient quantum yield for photocatalytic water

splitting can harvest only photons with energy above 500 nm (e.g., GaN:ZnO, BiVO₄ - SrTiO₃:Rh(La))^{3,4}. For biomedical applications, the generation of blue photons is again important to trigger photoinduced drug delivery, photo-dynamic therapy and for optogenetics. In addition, for these applications it is crucial to utilizing near-infrared (NIR) photons to drive the upconversion, as the window for high transparency of biological tissue lies in the NIR region (700 - 900 nm).^{1,5-8} While there are many systems

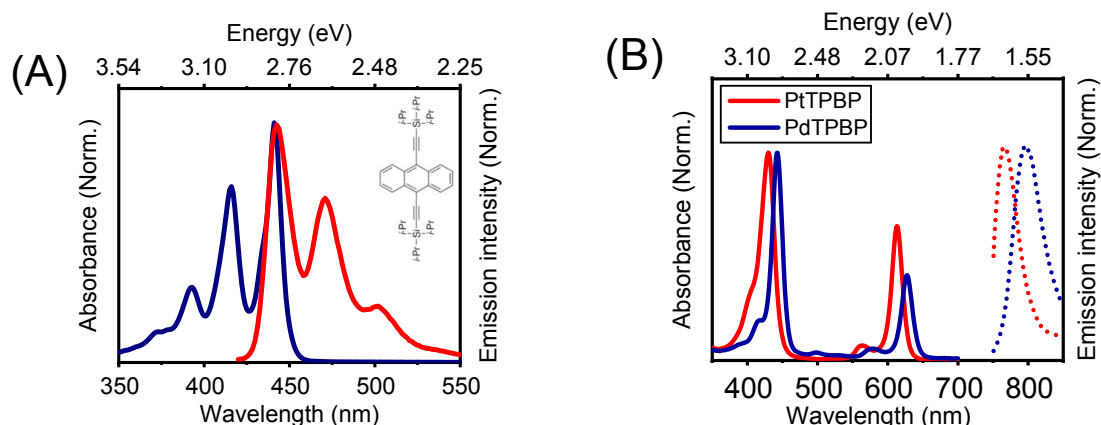


Figure 1. (A) absorption (blue) and emission (red) spectra of diluted TIPS-Ac in toluene, (B) absorption spectra (left) and emission spectra (right) of PdTPBP (blue) and PtTPBP (red)

with PUC working in the NIR to red,^{5,9-13} or green to blue regions,¹³⁻¹⁷ there are few systems capable to functioning to convert NIR to blue photons.⁶⁻⁸

As the difference in energy between blue and NIR photons is large (e.g., 470 nm: 2.64 eV and 800 nm: 1.55 eV), a reduction of energy loss in PUC process, leading to larger anti-Stokes shift ($:(\text{PUC emission energy}) - (\text{excitation energy})$), is also important.⁶ However, achieving such a large anti-Stokes shift is extremely challenging and there have been very few reports of shifts greater than 1.0 eV.^{6,8} Crucially, there has been no report, to the best of our knowledge, of a material with an anti-Stokes shift greater than 1.0 eV that also has a linear excitation intensity dependency (slope 1 for the PUC process). The total energy loss in PUC processes arises from the following components: (1) energy loss from intersystem crossing (ISC) in the triplet sensitizer (S_1 sensitizer $\rightarrow T_1$ sensitizer), (2) energy loss involved with triplet energy transfer (TET) from the sensitizer to the emitter, (3) energy loss due to the driving force for the TTA process ($2T_1$ annihilator $\rightarrow S_1$ annihilator). To overcome (1), the losses associated with generation of triplets via ISC, there have been reports of direct excitation from S_0 to T_1 in molecules containing heavy atoms (e.g., osmium (Os) complex, or acenes with bromide (Br) chromophore). However, such materials have not achieved an anti-Stokes shift of 1.0 eV or above with a linear excitation intensity dependency.⁵⁻⁸

One of the keys to reduce loss in energy for PUC is to minimize the driving force of TTA process (i.e., process (3): difference in energy between $2T_1$ and S_1 of TTA material). Reports of annihilators fluorophores which can accept low-energy triplets (< 1.55 eV) and generate blue light have so far mainly focused on 9,10-Bis(phenylethynyl)anthracene (BPEA)¹⁸⁻²³ and perylene derivatives.^{1,7,24} However, these materials function with low efficiency of TTA (e.g., BPEA)¹⁸⁻²⁰ and/or require large driving force for TTA (e.g., perylene derivative: $2T_1 - S_1 \approx 0.38$ eV)^{1,7,24}. Therefore, there is a clear need for PUC materials with a large anti-Stokes shift as well as efficient PUC from NIR to blue.

Herein, we show efficient TTA ($\Phi_{\text{TTA}} = 77 \pm 3\%$) in 9,10-Bis[(triisopropylsilyl)ethynyl]anthracene (TIPS-Ac) which can accept NIR energy and generate blue light (ca. 470 nm). We demonstrate that the TTA process occurs efficiently, despite a relatively small driving force of less than 0.32 eV. This enables a large anti-Stokes shift of 1.03 eV, when the triplet state of the sensitizer is directly excited with NIR light (at 785 nm).

Figure 1A shows absorption and emission spectra of diluted TIPS-Ac in toluene. TIPS-Ac possesses S_1 energy of 2.78 eV, which was estimated with extrapolation of the absorption spectrum, and emission with peaks at 430 nm (0-0), 470 nm (0-1), and 500nm (0-2).²⁵⁻²⁹ The photoluminescence quantum yield (PLQY) of a 1 mM TIPS-

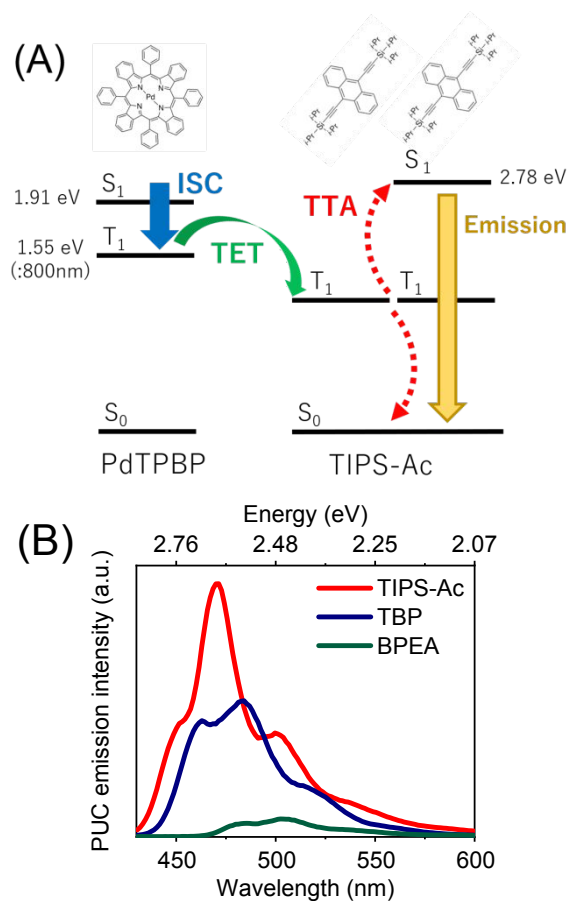


Figure 2. (A) Scheme of PUC with TIPS-Ac and PdTPBP via ISC triplet sensitization, (B) PUC emission spectra of solution containing 1 mM TIPS-Ac, TBP, or BPEA and 20uM PdTPBP excited at 635 nm with power density of 6.0 mW cm^{-2}

Ac toluene solution was measured to be $75 \pm 2 \%$, when excited at 405nm.³⁰

We begin by investigating the TTA properties of TIPS-Ac, using a conventional sensitization process. Pd(II) meso-Tetraphenyl Tetrabenzoporphine (PdTPBP) is a porphyrin based triplet sensitizer which generate triplet excitons via ISC.³¹ The absorption and emission spectra of PdTPBP is depicted in Figure 1B. Figure 2A shows the PUC scheme. We compare TIPS-Ac with BPEA and 2,5,8,11-Tetra-tert-butylperylene (TBP: a perylene derivative with high solubility in non-polar solvents) using the same sensitizer and the concentration. Figure 2B depicts PUC spectra of solutions consisting of 1 mM TIPS-Ac, BPEA, or TBP, and 20 uM PdTPBP with an excitation at 635 nm of 6.0 mW cm^{-2} . All samples generated PUC emission. However, under the same excitation conditions, the sample with TIPS-Ac generated the brightest emission of the three. The upconversion quantum yield (UCQY) for TIPS-Ac, TBP,

Table 1. Parameters of PUC with TIPS-Ac, TBP, or BPEA and PdTPBP excited at 635 nm

Sample	Φ_{UC} (%)	Φ_{ISC} (%)	Φ_{TET} (%)	Φ_{FL} (%)	Φ_{TTA} (%)
TIPS-Ac + PdTPBP	27 ± 0.5	97	97	75 ± 2	77 ± 3
TBP + PdTPBP	17.9	97	93	94	42
BPEA + PdTPBP	2.0	97	100	85	4.9

BPEA are measured to be $27 \pm 0.5 \%$, 17.9% , 2.0% , respectively, against a maximum of 50% due to the two-photon nature of the process. We note that the UCQY was measured relative to BPEA in degassed toluene, which showed a PLQY of 85% ¹⁹. The obtained PUC PLQY of 2.0% in the BPEA system is similar to previous reports.^{18,19} Table 1 lists the parameters of the PUC calculated with the following equation (1).

$$\Phi_{UC} = 1/2 \Phi_{ISC} \times \Phi_{TET} \times \Phi_{TTA} \times \Phi_{FL} \quad (1)$$

The Φ_{UC} , Φ_{ISC} , Φ_{TET} , Φ_{TTA} , and Φ_{FL} are represented as UCQY, ISC efficiency, TET efficiency, TTA efficiency, and PLQY of emission from the emitter (annihilator in this work), respectively. The Φ_{ISC} was taken to be 0.97 based on previous work.³¹ Φ_{TET} was estimated via the quenching of phosphorescence at around 800 nm from PdTPBP in the presence of each annihilator. TET from PdTPBP (T_1 of 1.55 eV) to TIPS-Ac was as efficient as 97% , with negligible back-transfer in the quasi-steady state, suggesting that the triplet energy of TIPS-Ac lies below 1.55 eV . Also, since the TTA process occurs efficiently, the $2T_1$ energy is estimated to be larger than the S_1 energy (2.78 eV). We therefore estimate the triplet energy of TIPS-Ac to be in the region of $1.39 - 1.55 \text{ eV}$. This suggests a driving energy for the TTA process in the region of $0 - 0.32 \text{ eV}$. We note that direct phosphorescence measurements of the TIPS-Ac were inconclusive on the triplet energy.

The estimated TTA efficiency of TIPS-Ac ($77 \pm 3 \%$) is highest in the series of the materials measured here, with TBP of 42% , BPEA of 4.9% . This is despite the relatively small driving force, compared to conventional TTA material converting from NIR to blue, for TTA in TIPS-Ac ($2T_1 - S_1 < 0.32 \text{ eV}$). This paves the way for the use of TIPS-Ac as an efficient TTA material which could achieve a large anti-Stokes shift and be capable of PUC from the NIR to blue. We note that all measurements in Figure 2B and Table 1 were carried out in quasi-linear regime (slope of ca. 1.2), where TTA efficiency is maximized. The PUC in emission intensity vs excitation power density data are shown in Figure S1. We also note that while the numbers of Φ_{FL} in TBP and BPEA in Table 1 were taken from literatures^{7,19}, our absolute measurement for fluorescence resulted in similar numbers to the literatures (TBP: 89% , BPEA: 82%), and hence, what we are proving of high efficiency in TTA with TIPS-Ac here is evidenced.

In order to demonstrate the utilization of NIR photons for PUC with TIPS-Ac annihilator, a triplet sensitizer with heavier atom was used in the PUC system. Pt(II) meso-Tetraphenyl Tetrabenzoporphine (PtTPBP) is known for generating triplet exciton via ISC, with a T_1 energy of around 1.61 eV judged from energy of the phosphorescence at room temperature³² (Figure 1B).

Here, we have found another route to generate triplet in PtTPBP. The absorption spectrum of PtTPBP solution in NIR region (Figure S2A) has a broad absorption with a peak at around 755 nm ($1.64 \pm 0.6 \text{ eV}$), with linear dependence of optical density on the concentration (Figure S2B). This is assigned as the S_0 - T_1 transition in PtTPBP, allowing us to directly excite the triplets with NIR photons, followed by the PUC, as shown in Figure 3A.

Figure 3B shows the PUC emission spectrum of a solution consisting of 1 mM TIPS-Ac and 1 mM PtTPBP, filled in a 1 mm path length cuvette, excited at 785 nm . In the PUC emission spectrum, the peak at around 785 nm was derived from the scattering of the excitation laser. PUC emission with a peak at 475 nm arising from TIPS-Ac was observed. This constitutes an anti-Stokes shift of 1.03 eV . The apparent slight red shift from the original (0-1) emission at 470 nm to the observed 475 nm was likely due

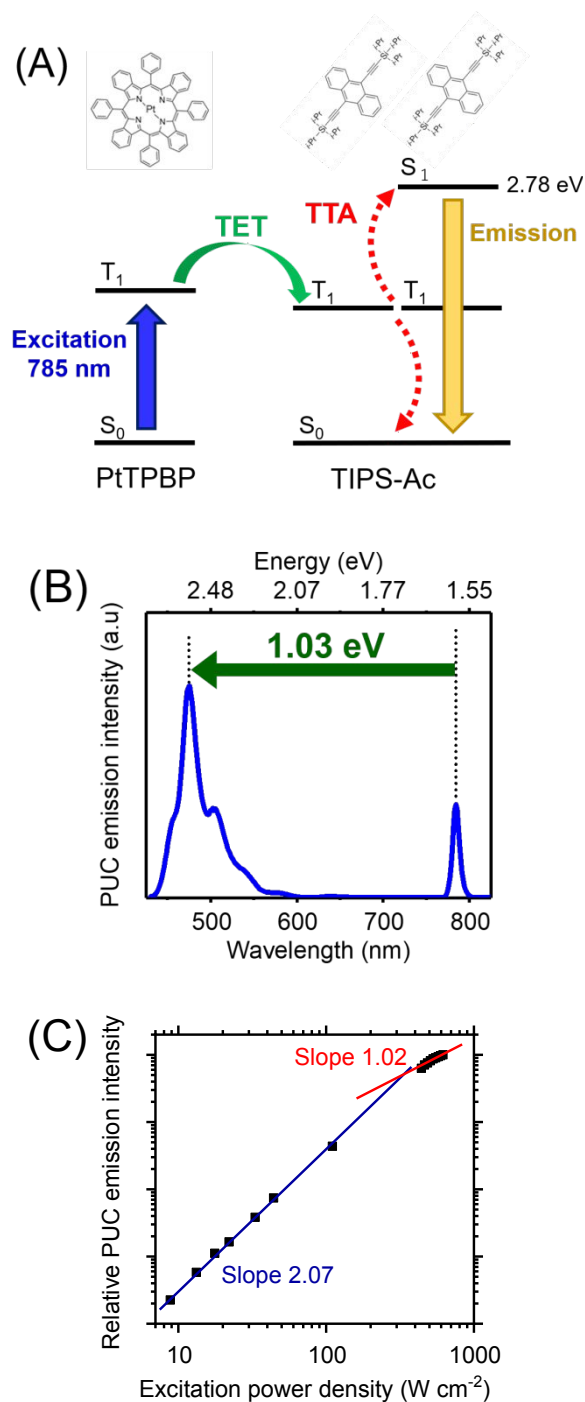


Figure 3. (A) Scheme of PUC with TIPS-Ac and PtTPBP via direct triplet sensitization, (B) PUC emission spectra of solution containing 1 mM TIPS-Ac and 1 mM PtTPBP excited at 785 nm , (C) relative PUC emission intensity against excitation power dependency of 1 mM TIPS-Ac and 1 mM PtTPBP excited at 785 nm

to reabsorption by TIPS-Ac and/or PtTPBP. Although the (0-0) emission (at 430 nm) of TIPS-Ac was almost completely suppressed due to reabsorption, the anti-Stokes shift achieved is over 1.0 eV. This is made possible by the relatively small driving force for TTA ($2 T_1 - S_1 < 0.32$ eV) compared to conventional TTA material such as TBP ($2 T_1 - S_1 \approx 0.38$ eV). Figure 3C shows the excitation power dependence of the TIPS-Ac - PtTPBP system. In the dependence, a change in the slope from square (2.07) to near linear (1.02) was observed, which is an evidence for TTA PUC. This is, to the best of our knowledge, the first report to achieve anti-Stokes shift of over 1.0 eV with a linear slope in excitation power dependence. Also importantly, the 785 nm excitation used lies directly in the biological transparency window (700 - 900 nm), allowing for long penetration depths.

We note that no contribution of two photon absorption was observed, as judged by measurement with 1 mM TIPS-Ac solution, as a reference sample, excited at 785 nm with the power density of ca. 620 W cm^{-2} , which is the maximum in Figure 3C. The estimated PUC PLQY of a solution consisting of 1 mM TIPS-Ac and 1mM PtTPBP system with an excitation at 785 nm (i.e., via direct triplet excitation) was 2.1 %. As a control measurement, the same solution (i.e., 1 mM TIPS-Ac and 1mM PtTPBP) was excited at 635 nm (i.e., triplet generation via ISC) and resulted in a UCPY of 4.4 % (this excitation power dependency: Figure S3).

At a high concentration of the triplet sensitizer, quenching of annihilator would occur (i.e., TTA material), resulting in a decrease in UCQY.^{19,33} While excitation conditions are different between continuous wave laser and pulse laser, time resolved emission measurement (supporting S4) indicates rate constant of quenching for the annihilator (TIPS-Ac) by the sensitizer (PtTPBP) was estimated to be $k_q = 8.0 \pm 0.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. Therefore, most of the drop over 75 % in the UCQY from the sample with 20 μM PdTPBP (27 ± 0.5 %) to the sample with 1 mM PtTPBP (4.4 %) was due to quenching of annihilator by high concentration of the sensitizer. Self-annihilation of PtTPBP with the high concentration may also reduce the TET efficiency as the high concentration resulted in shorter lifetime of the phosphorescence (supporting S4). Besides, part of the decrease in the UCQY could also be attributed to reabsorption by the concentrated PtTPBP. On the other hand, the difference in the PLQY with 1 mM PtTPBP between direct triplet excitation (2.1 %) and via ISC (4.4 %) was mainly due to reabsorption. For application to bio-imaging and/or drug delivery, the upconverter material would be packed in space of 100 μm order size, for example in capsule delivered to a specific region of the body.^{22,23} For such applications, thus, reabsorption would be reduced and the 1 mM TIPS-Ac and 1 mM PtTPBP would show PUC PLQY with NIR excitation as low as 4.4 % or higher than that since even at 635 nm the experimental optical density of the sample was ca. 0.4, which is still capable of inducing significant reabsorption.

A prominent feature of this work is that we show TIPS-Ac to be a highly efficient TTA material ($\Phi_{\text{TTA}} = 77 \pm 3$ %), which is higher than BPEA (4.9 %) and diphenyl anthracene (DPA, ~ 50 %)¹⁹, despite their similar molecule structures. While there is an active debate in the literature

as to the cause of these varying efficiencies it is worth noting the suggestion that a possible loss pathway for BPEA could be access to the T_2 state via TTA.³⁴ There is also the possibility of tuneable energies in the excited states due to the rotation of the ethynyl - phenyl chromophore, which could cause multi-molecule interactions involved in intermediate states in TTA process to relax in an unfavorable manner.¹⁹ To understand the energetic structure of TIPS-Ac we have performed electronic structure calculations, to obtain the energy levels for this system. We find that TIPS-Ac has larger T_2 energy than twice of T_1 energy ($T_2 - 2T_1 = 0.06 - 0.83$ eV, Table S3), which is very important to reduce losses in the TTA process, as the T_2 state is not accessible. Compared to DPA, TIPS-Ac possesses a more rigid bonding in ethynyl group and more symmetric structure, which may reduce non-radiative loss pass in the TTA process. Besides, the (triisopropylsilyl)ethynyl group would lead to preferable bi-molecule separation to proceeding TTA. These features may contribute to the higher TTA efficiency than DPA.

In conclusion, we have demonstrated PUC from NIR to blue photons with TIPS-Ac as an annihilator. Exciting PdTPBP at 635 nm, generating triplets via ISC, showed a PUC PLQY with TIPS-Ac of 27 ± 0.5 % with a TTA efficiency of 77 ± 3 %, despite a relatively small driving energy for the TTA of less than 0.32 eV. Utilizing direct triplet generation in PtTPBP via 785 nm excitation allowed for PUC with an anti-Stokes shift of 1.03 eV to be achieved. The PLQY was reduced due to reabsorption losses with the measurements here, but for applications using sub-micro size, such as bio-imaging and drug delivery, these reabsorption effects would be reduced. As another strategy to overcome reabsorption losses, TIPS-Ac itself can function as photocatalyst²⁶. These results suggest that direct excitation of triplets with NIR photons, combined with novel TTA emitters with low driving energies for TTA, yet capable of high PUC efficiency, offers a promising route to efficient NIR to blue upconversion.

ASSOCIATED CONTENT

The supporting information is available free of charge via the Internet at <http://pubs.acs.org>.

Experimental methods, excitation power dependence on PUC emission from TIPS-Ac, TBP, or BPEA and PdTPBP system, absorption spectrum of PtTPBP

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Notes

The authors declare no competing financial interest

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