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Heavy atom-free triplet photosensitizer based on thermally activated delayed fluorescence material for NIR-to-blue triplet-triplet annihilation upconversion

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ABSTRACT

Triplet-triplet annihilation (TTA) upconversion-based materials have potential application in the broad range of research areas, including photocatalysis and life sciences. However, near-infrared (NIR)-to-blue upconverted emission is preferred for most of the practical applications, but developing a NIR-to-blue TTA upconversion system is a challenging task in photochemistry. In this work, a thermally activated delayed fluorescence (TADF) material with intense visible-to-NIR absorption is demonstrated that shows a longer triplet state lifetime (32 µs) and high triplet state energy ($E_T = 1.55$ eV). For the first time, a heavy atom-free NIR ($\lambda_{ex} > 650$ nm) to blue ($\lambda_{em} < 460$ nm) TTA upconversion system was devised, employing the dimeric borondifluoride curcuminoid TADF material as triplet photosensitizer (PS) and a large anti-Stokes shift (0.88 eV) along with moderate upconversion yield was achieved. Our work provides the solution and guidance for the future development of purely organic heavy atom-free NIR activating TTA upconversion system for a wide array of applications.

Photon upconversion, an anti-Stokes shift process that initiates upon exciting the photosensitizer (PS) with low energy photon and produces the upconverted high energy photon, has gained considerable attention in photovoltaics because of its potential to improve the efficiency of solar-powered devices [1,2]. Among the various upconversion approaches, the triplet-triplet annihilation (TTA) upconversion is of particular importance, as it can be accomplished using the low power non-coherent excitation source, for instance, sunlight [3–5]. TTA upconversion has proven to be useful in a wide range of processes/applications, including the biological imaging [6,7], photocatalysis [8,9], data storage and most importantly in photovoltaics to maximize the solar cell efficiency by overcoming the Shockley–Queasier limit [10,11]. To date, several TTA upconversion systems have been introduced to maximize the utilization of solar energy by achieving the large anti-Stokes shift [1], but developing the near-infrared (NIR)-to-blue upconversion system remains challenging. However, the NIR-to-blue TTA upconversion is highly important and desired for various applications, ranging from drug release [12,13], organic decomposition to photocatalysis [9,14].

TTA upconversion comprises of two primary components, *i.e.*, triplet PS and triplet acceptor and is accomplished in the following sequential process [15–17]. Firstly, the PS harvests the excitation energy and produces the triplet-excited state through the intersystem crossing (ISC), which is then transferred to the triplet acceptor. Afterward, the upconverted emission is generated by a triplet acceptor following the TTA process. Thus, designing the triplet PS and acceptor with a suitable triplet (T_1) energy level is the basic requirement of TTA upconversion. However, developing NIR activatable triplet PS with a higher T_1 energy level is a challenging task. Up to now, several approaches, including the heavy atom-effect [18,19], symmetry breaking charge transfer and charge recombination induced ISC [20–22], have been adopted to access the triplet excited state in the organic compounds. But most of the triplet PSs based on heavy atom-effect face the problem of a short-lived triplet state or low T_1 energy level; thus, not very suitable for TTA upconversion [23–25].

An ideal PS for TTA upconversion should have a long-lived triplet state, strong NIR absorption, efficient ISC and higher T_1 energy level. Recently, few triplet PSs based on Os(II), Mo(0), Pd(II) and Pt(II) transition metal complexes have been investigated for TTA upconversion, and NIR-to-visible upconversion was achieved [1,26–28]. However, these metal complexes face the problem of

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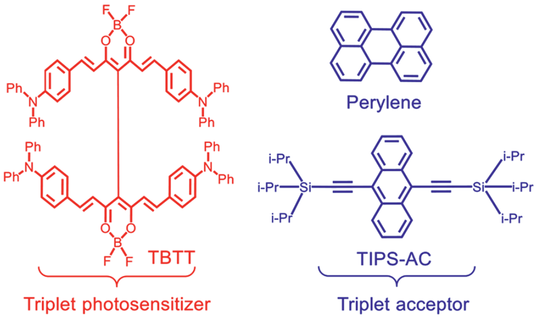

Scheme 1. The molecular structures of triplet photosensitizer (TBTT) and the triplet acceptor (perylene and TIPS-AC) used in the TTA upconversion.

either weak absorption in the NIR window, short triplet lifetime, or high cost, thus, are not ideal for TTA upconversion. Previously, Kimizuka introduced some NIR activatable TTA upconversion system, comprising of Os(II) derived PSs with direct S_0-T_1 absorption feature, exhibiting the large anti-Stokes shift. But the absorption of these PSs is very weak at the excitation wavelength (NIR window) [29]. Recently, attempts were made to improve the anti-Stokes shift of heavy atom-free TTA upconversion system by adopting several approaches; for instance, Zhao's research team introduced the tactic to improve the anti-Stokes shift taking advantage of the charge- transfer absorption band (longer wavelength) of donor-acceptor based PS [23]. At the same time, Peng's group implemented the thermally activated delayed fluorescence (TADF) material as PS and achieved the large anti-Stokes shift in TTA. However, absorption of the PS at the excitation wavelength is weak and limited to the visible region in all these systems. In recent years, Castellano developed a red-to-yellow TTA upconversion system based on heavy atom-free squaraine derivative, but the observed anti-Stokes shift (0.27 eV) is small due to low lying triplet energy level of PS [30]. In short, to date, there is no report available on the heavy atom-free NIR-to-blue TTA upconversion.

It is well-known that TADF chromophores have a small singlet-triplet energy gap (ΔE_{ST}), thus, are quite interesting for the application of TTA upconversion in terms of achieving large anti-Stokes shift and minimize the energy loss [31]. Using NIR activating TADF material in TTA upconversion can be one possible way to achieve heavy atom-free NIR-to-blue upconverted emission, however, NIR activating TADF material are rare. To address the above-mentioned challenge, herein, we introduced a NIR activatable dimeric boron-difluoride curcuminoid derivative (TBTT; Scheme 1) with TADF feature into TTA upconversion. The compound is reported, and previously it was investigated for the organic light-emitting diode (OLED) study by Adachi's group [32], but its photophysics, especially the triplet excited state properties, remained ambiguous. We found that the TBTT possess intense absorption in the NIR region. Theoretical computation and the low-temperature study of TBTT revealed a high T_1 energy level (*ca.* 1.55 eV), while the nanosecond transient absorption study confirmed the long-lived triplet state (32 µs). Considering these features, we implemented this NIR TADF compound as triplet PS and devised a new efficient NIR-to-blue TTA upconversion system. Notably, this is the first report of a heavy atom-free NIR-to-blue TTA upconversion system. Though the observed upconversion yield is not very high, might be due to the moderate ISC efficiency of TBTT, but it introduced the molecular design with higher T_1 energy which can be useful for the future development of NIR activating heavy atom-free triplet PSs. Moreover, the curcuminoid derivative's ISC efficiency may be further improved by adjusting the ΔE_{ST} *via* controlling the donor strength of the triphenyl unit through structural modification, which is under investigation.

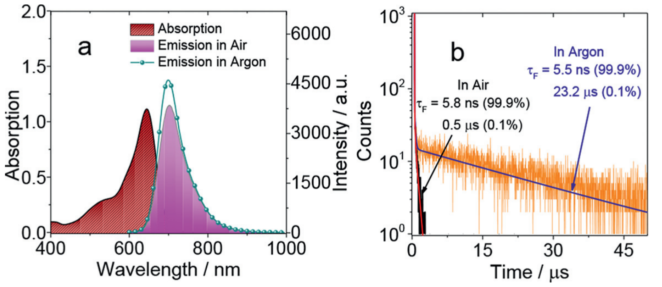

Fig. 1. (a) UV–vis absorption and steady-state fluorescence emission spectra of TBTT in toluene, λ_{ex}= 590 nm. (b) Fluorescence emission decay curves of TBTT (λ_{em} = 700 nm) in toluene under air and argon atmosphere, λ_{ex}= 640 nm, $c = 1.0 \times 10^{-5}$ mol/L, 20 °C.

The UV–vis-NIR absorption study showed that the TADF material TBTT absorbs in the broad region of the spectrum (orange-NIR) and possess an intense absorption band around 651 nm (1×10^5 L mol^{-1} cm^{-1}). The absorption of TBTT exhibited a slight bathochromic shift upon switching from non-polar to polar solvent; however, the intensity of absorption remained insensitive to polarity (Fig. S4a in Supporting information). The fluorescence emission investigation of curcuminoid derivative TBTT showed the NIR emission even in the non-polar solvent toluene (Fig. 1). The emission of TBTT showed the red-shifting and quenching upon increasing the solvent polarity, thus, confirming the intramolecular charge transfer (ICT) feature of the emissive state (Fig. S4b in Supporting information) [32].

Previously, the TADF was observed in the 4,4'-bis(*N*-carbazolyl)-1,10-biphenyl (CBP) blend thin film of TBTT [32]. To study its possibility in solution, the oxygen sensitivity experiment on the emission of TBTT was conducted which indicated the presence of some delayed (long-lived) component, as the emission intensity showed significant improvement in the deaerated solution (Fig. 1). This assumption was further verified by fluorescence lifetime study, as a longer lifetime of 23 µs was observed in deaerated solution compared to prompt fluorescence decay ($\tau_F = 5.8$ ns) in air (Fig. 1b). The concentration-dependent and power-dependent luminescence study was also conducted, which excluded the possibility of TTA delayed fluorescence (Fig. S5 in Supporting information) [33]. For further insight, low-temperature emission study and theoretical computation were performed, which revealed that the lowest triplet excited state (T_1) of TBTT is with slightly higher energy (1.55 eV) (Fig. S4c in Supporting information). Based on these results, we found a small singlet-triplet energy gap ($\Delta E_{ST} = 0.2$ eV) which is less than 0.3 eV, thus, confirming the TADF process in TBTT.

To get further insight into triplet excited state properties, the singlet oxygen sensitizing and nanosecond transient absorption studies of TBTT were conducted. TBTT showed a moderate sin-

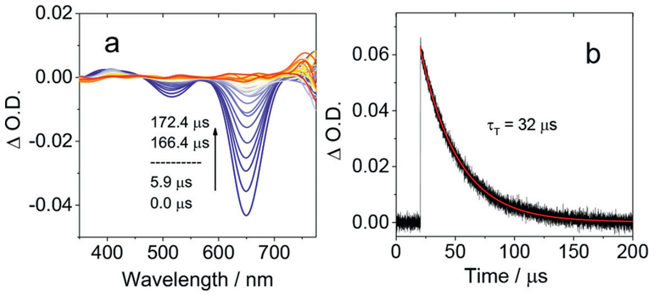

Fig. 2. (a) Nanosecond transient absorption spectra of TBTT at different delay time. (b) The decay curve of TBTT at 650 nm. λ_{ex}= 635 nm, in toluene, $c = 1.0 \times 10^{-5}$ mol/L, 20 °C.

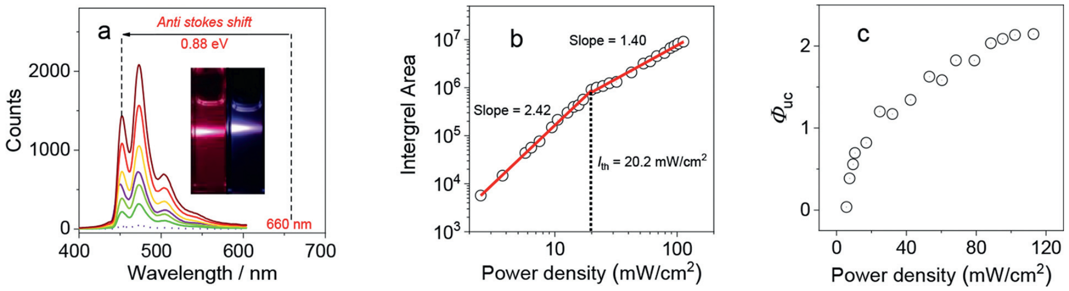

Fig. 3. (a) Power dependent upconverted luminescence spectra of TBTT (triplet photosensitizer) and TIPS-AC (triplet acceptor) in deaerated toluene under the variable-intensity of excitation source, c[TTBT] = 1×10^{-5} mol/L and c[TIPS-AC] = 1×10^{-4} mol/L, 20 °C. Inset: photographs of TBTT alone (red), and the upconversion of the TIPS-AC dyad in deaerated toluene (blue), $\lambda_{ex} = 660$ nm. (b) Integrated upconversion fluorescence emission intensity of TIPS-AC plotted as a function of incident power density. (c) Upconversion quantum yield of TIPS-AC plotted as a function of incident power density.

glet oxygen generation ability ($\Phi_{\Delta} = 21\%$) in toluene. The transient absorption profile of TBTT, obtained at 635 nm excitation (Fig. 2), showed a strong ground-state bleaching band (GSB) centered at *ca.* 650 nm, which is consistent with its absorption (Fig. S4a). The transient absorption spectra of TBTT also possess the weak broad excited state absorption (ESA) around 400 nm which extends upto NIR region, however, it is not obvious due to overlap with strong GSB. The triplet excited state lifetime of TBTT was obtained by monitoring the decay trace at the GSB band (650 nm). A longer lifetime of 32 µs, was observed in the deaerated environment, which was strongly reduced upon exposing the solution to air (0.2 µs), thus, confirming the triplet nature of the observed species [33]. The triplet lifetime of TTBT is quite longer than lifetime of previously reported red TADF material based on fluorescein derivative (2.6–22.1 µs) [30,34–38].

The strong NIR absorption, high triplet energy level and long-lived triplet state make the TBTT quite interesting. Notably, most of the NIR activating PSs possess low lying triplet state energy level (<1.3 eV) [39–41], which restrict its application in several areas such as TTA upconversion. The above-mentioned fascinating features of TBTT get our attention to explore its application in TTA upconversion. Based on the predicted triplet energy level ($T_1 = 1.55$ eV) of TBTT by low temperature luminescence study, perylene ($T_1 = 1.53$ eV) was selected as triplet acceptor, and upconversion was performed [42,43]. Upon exciting the mixture of TBTT and triplet acceptor perylene with NIR laser (660 nm), an upconverted emission around 445 nm was observed (Fig. S8 in Supporting information). However, a moderate upconversion quantum yield (Φ_{UC}) of 0.8% was observed (Note that, the upconversion quantum yield is normalized upconversion intensity, a factor of 2 was used in the calculation). For further insight, the quenching study by intermolecular triplet-triplet energy transfer (TTET) among the upconversion pair (TBTT PS and perylene acceptor) was conducted (Fig. S6 in Supporting information). A high TTET efficiency up to 95% was observed at the 0.1 mmol/L concentration of acceptor with a large Stern-Volmer quenching constant ($K_{SV} = 1.8 \times 10^5$ L/mol) and bimolecular rate constant ($K_q = 5.62 \times 10^9$ L mol^{-1} s^{-1}). Based on these results, we assumed that the TTET between TBTT and perylene is efficient, thus low Φ_{UC} is probably due to low TTA efficiency ($\Phi_{TTA} = 4.7\%$) of perylene in this upconversion system.

To verify this assumption and improve the Φ_{UC}, we performed the TTA upconversion using the 9,10-bis[((triisopropyl)silyl) ethynyl]-anthracene (TIPS-AC) as triplet acceptor (Fig. 3). As previous report on the TIPS-AC showed that it has high TTA efficiency, which can be effective to improve the Φ_{UC} [44]. Interestingly, we found that with TIPS-AC as a triplet acceptor, the Φ_{UC} of TBTT improved to 2.15%, although the TTET efficiency among TBTT and TIPS-AC is lower ($\Phi_{TTET} = 86\%$) as compared to that of with perylene ($\Phi_{TTET} = 95\%$). For further insight, TTA efficiency of TIPS-AC in the current system was calculated [9], and as expected, high $\Phi_{TTA} = 16\%$ was observed, which is nearly three-fold to that of perylene. Though the upconversion quantum yield is moderate in the current system but is with several advantages compared to the conventional NIR-to-blue TTA upconversion system comprising of Os(II), Pd(II), Pt(II) and Mo(0) based metal complexes [27,28,44,45], for instance, the simple and cost-effective synthetic route of TBTT, strong absorption, long-lived triplet state (several times longer compared to Os(II) and Mo(0) based PSs triplet lifetime) and low power excitation. Moreover, we also performed the TTA upconversion using the 721 nm laser as an excitation source and upconverted emission of TIPS-AC was observed (Fig. S9b in Supporting information), however, the upconversion intensity was quite weak due to the weak absorption of compounds.

In summary, we demonstrated the first example of heavy atom-free near-infrared ($\lambda_{ex} > 650$ nm) to blue triplet-triplet annihilation (TTA) upconversion taking advantage of small ΔE_{ST} of thermally activated delayed fluorescence (TADF) material. The TADF material based on dimeric borondifluoride curcuminoid derivative shows the strong absorption ($\varepsilon = 108{,}000$ L mol^{-1} cm^{-1}), long-lived triplet state (32 µs), moderate ISC efficiency ($\Phi_{\Delta} = 21\%$) with high triplet state energy ($E_T = 1.55$ eV). These features made it worthy for TTA upconversion and contributed to achieve the large anti-Stokes shift of 0.88 eV. Silyl-substituted anthracene derivative (TIPS-AC) was found to be better triplet acceptor for this upconversion system compared to conventional triplet acceptor perylene due to high Φ_{TTA} and 2.15% upconversion quantum yield was achieved. This study will be useful for the future design of heavy atom-free TTA upconversion systems for photocatalytic devices and biomedical applications.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2022.05.029.

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