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Organic Triplet Sensitizer Library Derived from a Single Chromophore (BODIPY) with Long-Lived Triplet Excited State for Triplet−Triplet Annihilation Based Upconversion

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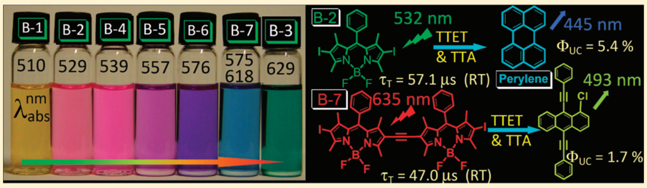
S Supporting Information



ABSTRACT: Triplet−triplet annihilation (TTA) based upconversions are attractive as a result of their readily tunable excitation/emission wavelength, low excitation power density, and high upconversion quantum yield. For TTA upconversion, triplet sensitizers and acceptors are combined to harvest the irradiation energy and to acquire emission at higher energy through triplet−triplet energy transfer (TTET) and TTA processes. Currently the triplet sensitizers are limited to the phosphorescent transition metal complexes, for which the tuning of UV−vis absorption and T_1 excited state energy level is difficult. Herein for the first time we proposed a library of organic triplet sensitizers based on a single chromophore of boron-dipyrromethene (BODIPY). The organic sensitizers show intense UV−vis absorptions at 510−629 nm (ε up to 180,000 M^{-1} cm^{-1}). Long-lived triplet excited state (τ_T up to 66.3 μs) is populated upon excitation of the sensitizers, proved by nanosecond time-resolved transient difference absorption spectra and DFT calculations. With perylene or 1-chloro-9,10-bis(phenylethynyl)anthracene (1CBPEA) as the triplet acceptors, significant upconversion (Φ_{UC} up to 6.1%) was observed for solution samples and polymer films, and the anti-Stokes shift was up to 0.56 eV. Our results pave the way for the design of organic triplet sensitizers and their applications in photovoltaics and upconversions, etc.

1. INTRODUCTION

Upconversion (UC), i.e., gain of emission, or more generally, population of excited states at higher energy upon photoexcitation at lower energy, has attracted much attention due to its potential applications in photocatalysis, photovoltaics (e.g., dye-sensitized solar cells), nonlinear optics, and molecular probes.[1−3] A few techniques are available for upconversion, e.g., by using two-photon absorption (TPA) dyes,[4,5] nonlinear optical crystals, such as potassium dihydrogen phosphate (KDP),[6] etc. However, these techniques suffer from some fundamental drawbacks. For example, coherent photoexcitation with very high power density is required for TPA upconversion, usually up to MW cm^{-2} (10^6 W cm^{-2}); note that terrestrial solar radiation is only 0.10 W cm^{-2} (AM1.5G), thus ruling out any applications of TPA upconversion with solar light as the excitation source.[7] Furthermore, it is difficult to tailor the molecular structures of the TPA dyes to optimize the upconversion wavelengths (energy levels) and at the same time maintain high TPA cross sections.

Recently a new method for upconversion emerged, i.e., the triplet−triplet annihilation (TTA) (Scheme 2), with which the above limitations can be addressed. Triplet sensitizer and acceptor are the two components of TTA upconversion. The excitation energy is harvested by triplet sensitizer, and the energy is transferred to triplet acceptor via triplet−triplet energy transfer (TTET). For detail photophysics, see the Jablonski diagram in Scheme 2.[8−10] The singlet excited state of the acceptor will be produced by annihilation of two acceptor molecules at triplet excited states, and finally the fluorescence of acceptor will be observed (Scheme 2). For this upconversion approach, the excitation/emission wavelength can be readily tuned simply by independent selection of triplet sensitizers/acceptors (but at least with the energy levels of the T_1 states of the sensitizer and acceptor matched, with the former appropriately higher than the latter).[8,9] This method is particularly promising because no coherent excitation is required, the excitation power can be down to a few mW cm^{-2}, and thus it is possible to use solar light as an excitation source.[8−11]

Currently the triplet sensitizers for TTA upconversion are limited to transition metal complexes, e.g., Ru(II) polyimine complexes[10a,12] or Pt(II)/Pd(II) porphyrin complexes.[1,13,14] Recently we proved that the long-lived ^{3}IL excited state is more efficient than the normal ^{3}MLCT excited state to sensitize TTA upconversion.[12b] A heavy atom is necessary for $S_1 \rightarrow T_1$ intersystem cross (ISC) (direct $S_0 \rightarrow T_1$ transition is forbidden).[15,16] Unfortunately, transition metal complex sensitizers are usually toxic and not cost-efficient. Furthermore, the significant challenge for the current sensitizers is the difficulty to modify the molecular structures to optimize the photophysical properties for upconversion purpose, such as excitation wavelength (absorption) and T_1 state energy levels. Actually, the currently available

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transition metal complex sensitizers are limited to off-the-shelf compounds and have been almost used up. It is urgent to develop alternative, more flexible molecular design rationales with which the related photophysical properties can be readily optimized by chemical modification.

Concerning this aspect, similar to the scenario of dye-sensitized solar cells (DSCs), we propose that organic triplet sensitizers will be the next generation sensitizers for TTA UC because they are more cost-efficient, environmentally benign, and most importantly easy to be derivatized to optimize the absorption wavelength and the T_1 state energy levels; all of these photophysical properties are crucial for TTA upconversion. However, design of organic sensitizers for TTA based UC is more challenging because the triplet excited state of the sensitizers must be populated (metal-free) upon excitation, instead of the singlet excited state for the organic sensitizers of DSCs.[7]

To the best of knowledge, however, no attempts have been made to develop organic triplet sensitizers with readily derivatizable molecular structures for TTA upconversion.[10c] Herein we report the first attempt to prepare a series of organic triplet sensitizers, derived from a single chromophore (boron-dipyrromethene, BODIPY). The absorptions of the sensitizers were readily tuned from green (510 nm) to red (629 nm) (ε up to 180,000 M^{-1} cm^{-1}). We observed very long room temperature (rt) triplet excited state lifetime (τ_T is up to 66.3 μs) for the organic sensitizers. Significant upconversions were observed with the organic sensitizers in both solution and polymer films, with upconversion quantum yields (Φ_{UC}) up to 6.1%.

2. RESULTS AND DISCUSSION

2.1. Design of the BODIPY-Based Organic Triplet Sensitizers. Our design of organic triplet sensitizers is inspired by the iodo-BODIPYs that show decreased fluorescence quantum yields (Φ_F) compared with the parent BODIPY, an indication of intersystem crossing (ISC).[17,18] BODIPY is particularly attractive because of their intense absorption of visible light, excellent photostability, and weak nonradiative decay of the excited state (high fluorescence quantum yields). Furthermore, the rich chemistry of BODIPY makes it possible to modify the molecular structure, and thus the energy levels of the S_1 and T_1 excited state can be fine-tuned.[19,20]

First we designed the mono- and bis-iodo-BODIPYs **B-1** and **B-2** (Scheme 1). The iodine atom is attached to the core of fluorophore, not the peripheral phenyl ring (**B-8**) (in this case iodo is not close to the π-conjugation core).[21] To shift the absorption to the red end, we designed **B-3** with an extended π-conjugation framework.[22a] **B-3** shows an absorption band at 629 nm, but our DFT calculation predicts a T_1 state of 1075 nm (1.15 eV) for **B-3**, too low for the available triplet acceptors, and thus, aided with DFT calculations, we designed **B-4**, **B-5**, **B-6**, and **B-7**, which show T_1 energy levels much higher than that of **B-3** (Table 1). These ethynylated BODIPY derivatives were prepared by Sonogashira coupling reactions with satisfying yields.

2.2. UV−vis Absorption and Fluorescence Spectra of the Sensitizers. UV−vis absorptions of the sensitizers cover a wide range from 510 to 629 nm (Figure 1). It should be pointed out that the absorption is intense, with molar extinction coefficients (ε) generally larger than 80,000 M^{-1} cm^{-1}. **B-2** shows red-shifted absorption (529 nm) compared with that of **B-1** (510 nm). For **B-3**, absorption at 629 nm was observed. Interestingly the absorptions of ethynylated sensitizers (**B-4** and **B-5**) cover the yellow region (529−557 nm). The absorption of **B-6** was extended to orange (576 nm) and shows an exceptionally high ε value (180,000 M^{-1} cm^{-1}), indicating efficient light-harvesting. Interestingly **B-7** shows red-shifted absorption (ε = 89,500 M^{-1} cm^{-1} at 618 nm) compared with that of **B-6**. This is the first report of a single family of organic triplet sensitizers that cover such a wide range of absorption wavelength.

The fluorescences of the sensitizers are at 532−706 nm (Figure 1b), but the fluorescence quantum yields (Φ_F) decreased with iodo substitution, for example, **B-1** and **B-2** show Φ_F of 0.036 and 0.027, respectively, vs Φ_F = 0.712 for **B-0** (Table 1). Decreased Φ_F is an indication of ISC, a prerequisite for the population of the T_1 state of the organic sensitizers upon photoexcitation. No phosphorescences were observed for these sensitizers.

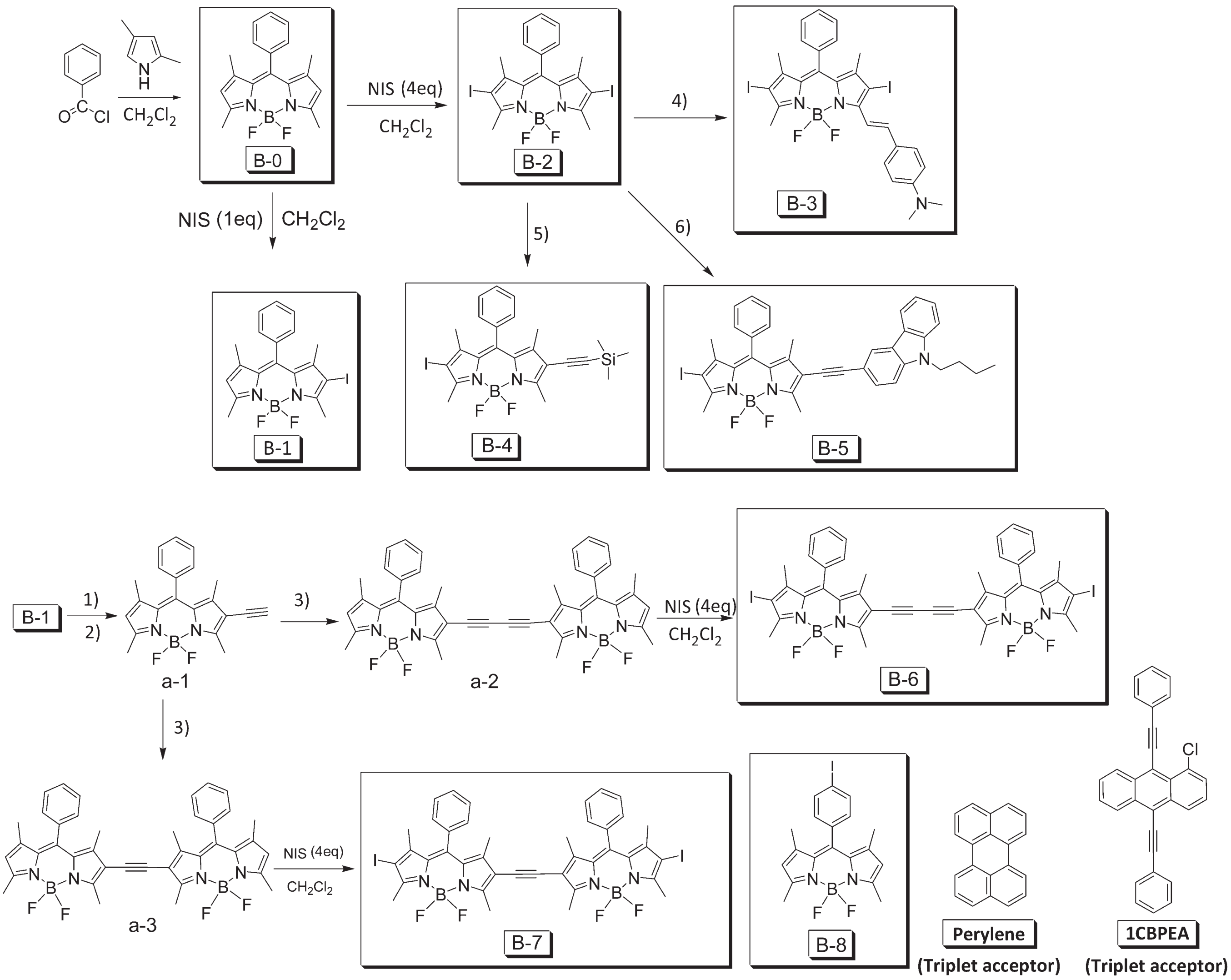
The emission spectra of the BODIPY derivatives at 77 K were studied (see Supporting Information). Weak emission bands in the range of 750−800 nm were found, which are attributed to the phosphorescence of the chromophores. This assignment is supported by the calculated energy level of the T_1 excited state of the BODIPY chromophores (Table 1). For example, emission bands at 752 and 785 nm were observed for **B-2** (Figure S72 in the Supporting Information), which are close to the calculated T_1 state energy level of 826 nm (Table 1).

2.3. Nanosecond Time-Resolved Transient Difference Absorption Spectra. Population of the triplet excited states of these organic sensitizers was proved by nanosecond time-resolved transient absorption spectroscopy (Figure 2). With pulsed excitation at 532 nm, significant bleaching at 520 nm was observed for **B-2**, as well as transient absorptions at 420 nm and 550−700 nm, which are characteristic for BODIPYs.[23,24] The transients are due to the absorption of the T_1 state (i.e., $T_1 \rightarrow T_2$, $T_1 \rightarrow T_3$, etc.) because formation of other species, such as a charge separated state, is unlikely.[23] This assignment is supported by DFT calculations (Supporting Information). The lifetime of the T_1 state of **B-2** (τ_T) is 57.1 μs, which is much longer than that observed with an Ir(III) complex that contains BODIPY subunit (τ_T = 25 μs).[24] For **B-1**, τ_T is even longer (66.3 μs). To the best of our knowledge, these are the longest rt triplet excited state lifetimes reported for BODIPY. Although the population of the triplet excited state of BODIPY has been observed with metal complexes,[23−25] this is the first time that the triplet excited state of BODIPY (metal-free) was observed with organic compounds.[17,19] Transients were also observed for **B-1** and **B-3**−**B-7** (Supporting Information).

2.4. DFT Calculations. The energy levels of the T_1 states of sensitizers are not readily available because these sensitizers are not phosphorescent at either room temperature or 77 K (see Supporting Information for the emission at 77 K). Thus we used density functional theory (DFT) and time-dependent DFT (TDDFT) calculations to predict the energy levels of the T_1 excited state. The energy levels of the T_1 states of the sensitizers are crucial for the TTA upconversion because an appropriate triplet acceptor can only be selected with the energy level of sensitizer known; the energy level of the acceptor has to be lower than the energy level of the triplet sensitizer.

For **B-1** and **B-7**, the T_1 energy levels were calculated as 1.51 and 1.43 eV, respectively (Table 1). For **B-0**, the T_1 energy is 1.52 eV (816 nm), which is close to the experimental value (1.61 eV, 770 nm), thus validating our theoretical approach of prediction of T_1 state energy levels. The selected frontier molecular orbitals (MOs) are presented in Figure 3 (for the MOs of

Scheme 1. Synthesis of the Organic Triplet Sensitizer Library (B-1−B-7)[a]



[a] The triplet acceptor perylene and 1-chloro-bis-phenyl ethynylanthracene (**1CBPEA**) were presented. The molecular structures of the reported compound **B-0**, **B-2** and **B-8** are included (**B-0** and **B-8** were not used as sensitizers). Reagents and conditions: 1) Trimethylsilylacetylene, Pd(PPh$_3$)$_2$Cl$_2$, PPh$_3$, CuI, NEt$_3$, reflux, 8 h; 2) NaOH(aq), THF/MeOH; 3) **B-1,** Pd(PPh$_3$)$_2$Cl$_2$, PPh$_3$, CuI, NEt$_3$, reflux, 8 h; 4) 4-(dimethylamino)-benzaldehyde, Piperidine, reflux; 5) Trimethylsilylacetylene, Pd(PPh$_3$)$_2$Cl$_2$, PPh$_3$, CuI, THF/NEt$_3$, r. t.; 6) 9-butyl-3-ethynylcarbazole, Pd(PPh$_3$)$_2$Cl$_2$, PPh$_3$, CuI, THF/NEt$_3$, rt.

other sensitizers, see Supporting Information). From the results of **B-3**, **B-5**, **B-6**, and **B-7**, the HOMO is distributed on the whole π-conjugated framework, but the LUMO is more localized (Figure 3). The red-shifted absorption of the sensitizers with larger π-conjugation framework can be rationalized by these MOs.

However, we noted that the BODIPY sensitizers with larger π-conjugation framework, such as **B-5**, **B-6** and **B-7**, show T$_1$ state energy levels similar to that of the parent compound. In order to investigate the origin of the apparent unexpected high T$_1$ state energy level of the sensitizers, the spin density of the sensitizers was investigated by optimization of the triplet state of the sensitizers. The spin density distribution of the selected sensitizers is presented in Figure 4.

Previously **B-8** was reported to show significant fluorescence ($\Phi_F = 0.69$), and thus **B-8** was used as triplet acceptor, not triplet sensitizer.[21] We attribute the nonefficient ISC of **B-8** to the distance between the heavy atom iodine and the fluorophore core of the BODIPY; the iodine is far away from the spin density surface (Figure 4). Clearly for the sensitizers we developed the heavy atom iodine is attached to the BODIPY core directly and the iodine is very close to the spin density distribution (Figure 4). Furthermore, we found that the spin density (namely, the T$_1$ excited state) of the **B-5**, **B-6**, and **B-7** is more localized, i.e., it is not distributed on the entire π-conjugation framework. Thus we expected the T$_1$ state energy level for these sensitizers would be similar to that of the parent compound **B-0** (800−900 nm). For **B-3**, however, the spin density is more delocalized and is spread over the whole π-conjugation framework, and thus the unique low T$_1$ state energy level of **B-3** (1075 nm) can be rationalized by its spin density distribution. The theoretical rationalization of the T$_1$ state energy level is helpful for design of organic triplet sensitizers. Usually with red-shift of the UV−vis absorption, the T$_1$ state energy level will decrease, which will frustrate the TTA upconversion. Sensitizers with red-shifted absorption but high T$_1$

Table 1. Photophysical Parameters of the Organic Triplet Sensitizers

	λ_{abs}[a]	ε[b]	λ_{em}	Φ_F (%)[d]	τ_F (ns)[e]	τ_T (μs)[f]	ΔE, $T_1 - S_0$[g]	Φ_{ISC}[i]
B-0	503	8.20	515	71.2 ± 0.4	3.86	0.02	816[h]	0.288
B-1	510	8.80	532	3.6 ± 0.3	0.16	66.3	819	0.964
B-2	529	8.90	552	2.7 ± 0.3	0.13	57.1	826	0.973
B-3[c]	629	7.28	706	9.5 ± 0.1	1.40	4.0	1075	0.905
B-4	539	7.54	563	7.8 ± 0.4	0.42	57.2	829	0.922
B-5[c]	557	5.94	631	4.6 ± 0.2	0.37	54.6	878	0.954
B-6[c]	576	18.0	623	10.5 ± 0.2	0.42	26.9	893	0.895
B-7[c]	575/618	9.09/8.95	646	9.3 ± 0.2	0.57	47.0	865	0.907

[a] In CH_3CN (1.0×10^{-5} M). In nm. [b] Molar extinction coefficient. In $10^4\ M^{-1}\ cm^{-1}$. [c] In toluene. [d] Fluorescence quantum yields. In CH_3CN. [e] Fluorescence lifetimes. [f] Triplet state lifetimes, measured by transient absorption. 1.5×10^{-5} M in CH_3CN. [g] The calculated energy gap between S_0 and T_1 state. In nm. [h] Experimental value: 770 nm. [i] Intersystem crossing efficiency, approximated by the Ermolev's rule. $\Phi_{ISC} = 1 - \Phi_F$.[22b,c]

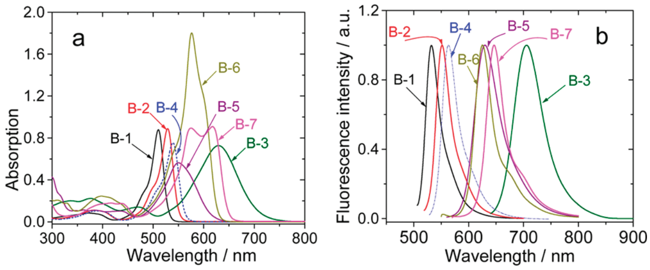


Figure 1. UV−vis absorption (a) and fluorescent emission (b) spectra of **B-1**, **B-2**, and **B-4** (in CH_3CN) and **B-3**, **B-5**, **B-6**, and **B-7** (in toluene); 1.0×10^{-5} M, 20 °C.

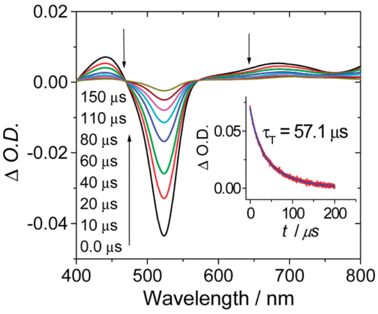


Figure 2. Nanosecond time-resolved transient absorption difference spectra of **B-2** in deaerated CH_3CN after pulsed laser excitation (λ_{ex} = 532 nm). Inset: decay trace of **B-2** at 525 nm; 1.5×10^{-5} M; 20 °C.

state energy level are beneficial for TTA upconversion. It is clear that our theoretical approach will be useful in the screening potential organic triplet sensitizers for TTA upconversions.

2.5. TTA Upconversion in Solution and Polymer Films with BODIPYs as the Triplet Sensitizers. The detail photophysics of TTA upconversion are presented in Scheme 2.[8−10] The critical photophysical properties of the sensitizer for TTA upconversion include the UV−vis absorption, the ISC, and the lifetime of the T_1 state of the sensitizers. Our new BODIPY sensitizers fulfill these requirements; for example, the sensitizers show intense absorption in the visible range and long-lived T_1 excited state.

The green-absorbing sensitizers **B-1**, **B-2**, and **B-4** give similar Φ_F, but the emission intensity varies drastically upon laser excitation at 532 nm (Figure 5a), which is due to the different ε values of the sensitizers at the excitation wavelength (Figure 1). The emissions of the triplet sensitizers in the presence of triplet acceptor (perylene) were studied (Figure 5b). Besides the prompt fluorescence emission of the sensitizers beyond 500 nm, the upconverted blue emission of perylene was observed (440−500 nm). Excitation of the sensitizers or perylene alone does not produce this emission band. **B-2** and **B-4** show similar upconversion. For **B-1**, however, the upconversion is weak. Upconversion quantum yield (Φ_{UC}) up to 6.1% was observed for **B-4**. Considering the intensive absorption of this sensitizer (ε is up to 5- or 10-fold of the normal transition metal complex sensitizers),[10c] the intensity of the upconverted emission is significant even with a Φ_{UC} value of 6.1%.

Interestingly, the fluorescence emission of the triplet sensitizers was not quenched at all in the presence of perylene (Figure 5b). This is reasonable since the triplet excited state of the sensitizer, not the singlet excited state, is involved in TTET (Scheme 2, Jablonski diagram).[10d] Thus, dual emissions were observed for the triplet sensitizers in the presence of triplet acceptor, i.e., the upconverted fluorescence of the triplet acceptor and the prompt fluorescence of the triplet sensitizers.

The potential of our organic triplet sensitizer approach is demonstrated by tailoring the molecular structure to readily switch the absorption from green to red. **B-3**, **B-5**, **B-6**, and **B-7** give absorption at 629, 557, 576, and 618 nm, respectively (Figure 1). **1CBPEA** was used as triplet acceptor (Scheme 1) (T_1 = 1.20 eV, 1036 nm). **B-3** shows intensive red-absorption, but no upconversion was observed, probably due to its low T_1 energy level. **B-7** shows significant upconversion of **1CBPEA** (Figure 6), due to its intense absorption. Furthermore, DFT calculations predict that **B-7** gives a T_1 energy level much higher than that of **B-3** (Table 1). The results demonstrated that these organic sensitizers can be used as promising prototypes for energy level tunable triplet sensitizers for TTA upconversion or other photophysical processes.

Previously 2,3-butanedione was used as organic sensitizer for TTA upconversion, but it was excited in blue region ($\lambda_{abs}{}^{max}$ = 417 nm), and the absorptions are extremely weak in the visible region (e.g., ε = 47 $M^{-1}\ cm^{-1}$ at 490 nm).[26] Furthermore, the Φ_{UC} is very low (0.5%). It should be pointed out that the absolute upconversion intensity is dependent on the absorption property of the triplet sensitizers. 2,4,5,7-Tetraiodo-6-hydroxy-3-fluorone (TIHF) was also used as organic triplet sensitizer,[27] but the τ_T of TIHF (25.0 μs) is much shorter than those of our triplet sensitizers (τ_T is up to 66.3 μs, Table 1), and a much smaller Φ_{UC} was observed (0.6%) for TIHF.[27] Moreover, it is difficult to modify the molecular structure of TIHF to optimize the absorption wavelength at which the TTA upconversion can be performed.

Interestingly, we observed a linear relationship between the upconverted fluorescence intensity and the excitation power (Figure 7). This is unusual since TTA based UC normally shows a quadratic relationship.[10d] Previously a linear relationship was reported for upconversion with Pt(II)octaethylporphyrin/DPA, and it was proposed to be due to the highly populated triplet excited state of the sensitizers and efficient TTET process.[28] Herein our new BODIPY organic sensitizers ensure efficient upconversion, i.e., intensive absorption (large ε) and efficient production (small Φ_F) of the long-lived triplet excited state (large τ_T). Upconversion with a linear relationship is more energy-efficient than with a quadratic relationship.

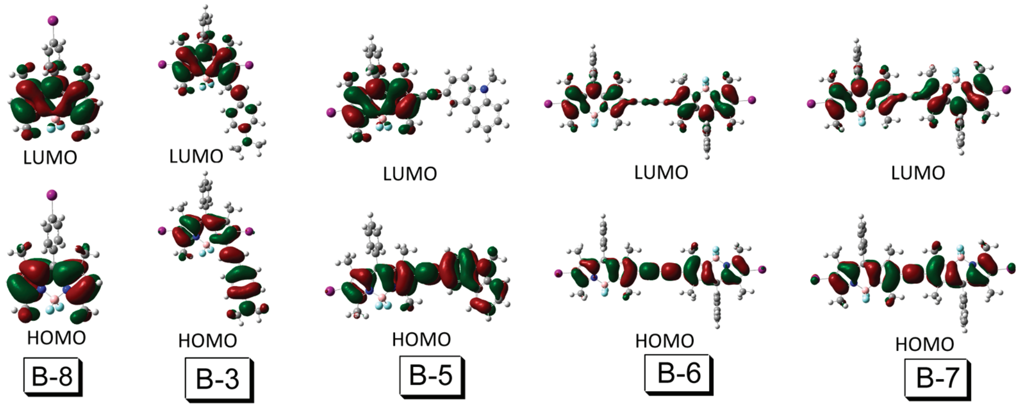


Figure 3. Selected frontier molecular orbitals involved in the vertical excitation and the triplet excited state (T1) of the sensitizers. The results of **B-8** are presented for comparison. The calculations are based on the optimized ground state geometry (S_0 state) at the B3LYP/6-31G(d)/ level using Gaussian 09W.

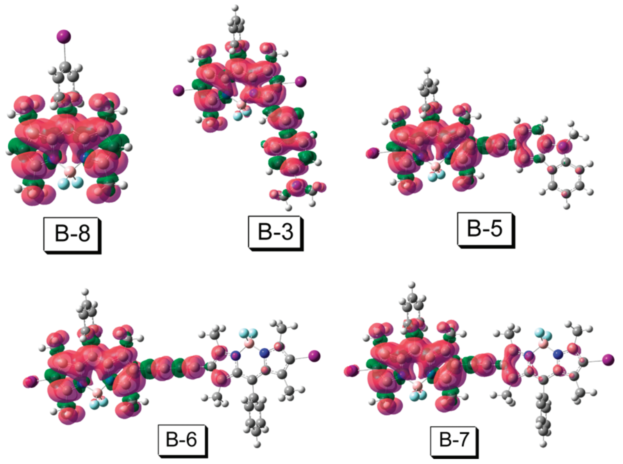
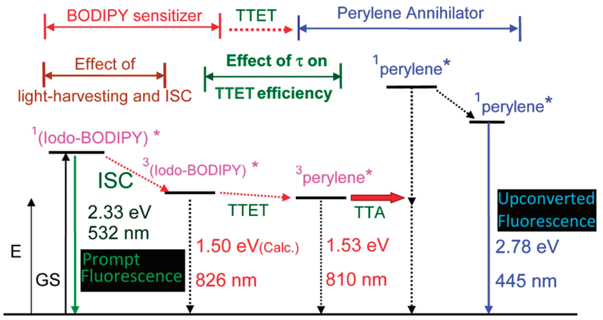


Figure 4. Isosurfaces of spin density of **BODIPY** sensitizers and the model compound **B-8** at the optimized triplet state geometries (isovalue = 0.0004). Calculation was performed at B3LYP/6-31G(d) level with Gaussian 09W.

Scheme 2. Jablonski Diagram of Triplet−Triplet Annihilation (TTA) Upconversion with Iodo-BODIPYs as Triplet Sensitizers[a]



[a] The triplet states of sensitizers and acceptors are non-emissive. TTET stands for triplet−triplet energy transfer. Exemplified by **B-2**.

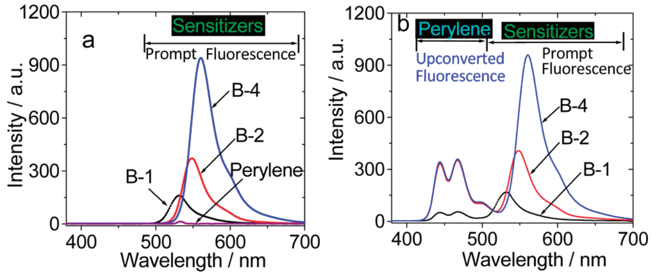


Figure 5. Upconversions with sensitizers **B-1**, **B-2**, and **B-4**. (a) Fluorescence emission of the sensitizers and perylene alone. (b) Emission of the sensitizers in the presence of perylene. Excited with 532 nm laser (5 mW, power density is 70 mW cm^{-2}). [Sensitizer] = 1.0×10^{-5} M; [perylene] = 1.1×10^{-4} M; in deaerated CH_3CN, 20 °C.

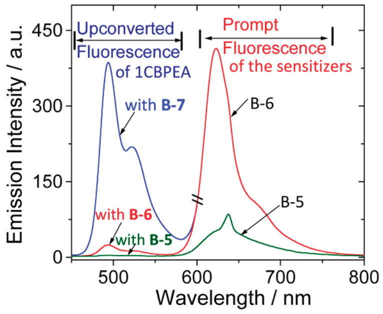


Figure 6. Upconversion with the red-absorbing organic triplet sensitizers **B-5**, **B-6**, and **B-7** with **1CBPEA** as acceptor (excited with 635 nm laser, 40 mW, power density is 141 mW cm^{-2}). Note the residual fluorescence of **B-7** is omitted. In deaerated toluene. [Sensitizer] = 1.0×10^{-5} M; [**1CBPEA**] = 2.0×10^{-5} M; 20 °C.

We performed the upconversion in polymer films (with PEG-1500 as the matrix) (Figure 8).[10d] For **B-4**, the fluorescence of **B-4** and the upconverted fluorescence of perylene were observed simultaneously (under air condition). Note that the relative intensity of the upconverted fluorescence vs the emission of **B-4** is more significant than that in solution (Figure 8a). Similar results were observed for **B-7** (Figure 8b) and other sensitizers (Supporting Information). For **B-7**, the prompt fluorescence was omitted. We did not measure the upconversion quantum yields in polymer films, but it was noted that the upconversion emission intensity is comparable to the fluorescence emission of the

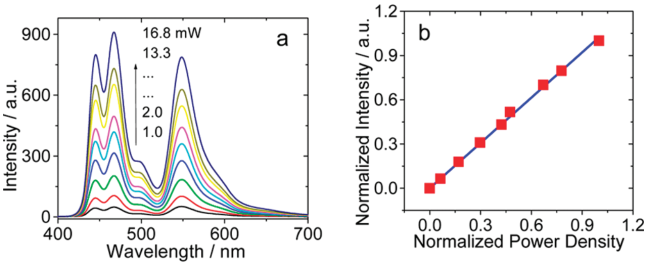


Figure 7. (a) Excitation power dependency of the upconverted perylene emission with **B-2** as sensitizer (λ_{ex} = 532 nm) in CH_3CN. (b) The normalized integrated emission intensity plotted as a function of normalized incident light power. The minimal and the maximal excitation power densities are 14.2 and 237.8 mW cm^{-2}, respectively. [Sensitizer] = 1.0×10^{-5} M; [perylene] = 1.1×10^{-4} M; 20 °C.

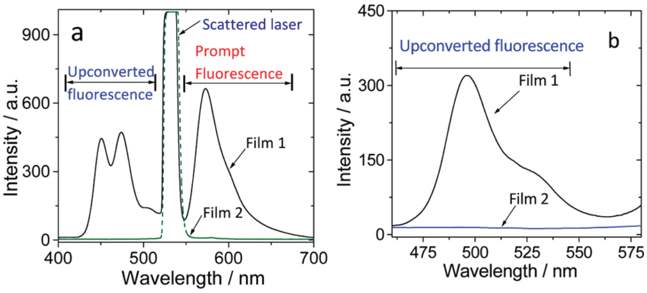


Figure 8. (a) Upconversion of **B-4**/perylene in PEG1500 polymer films under air condition. For film 1, **B-4** and perylene were mixed. Sensitizer/acceptor/polymer = 33 μg/176 μg/165 μg. For film 2, only perylene was used. λ_{ex} = 532 nm, 5 mW, 20 °C. (b) Upconversion of **B-7**/**1CBPEA** in PEG1500 polymer films under air condition. For film 1, **B-7** and **1CBPEA** were mixed. Sensitizer/acceptor/polymer = 55 μg/288 μg/165 μg. For film 2, only **1CBPEA** was used. Note the prompt fluorescence of the sensitizers is omitted in (b). λ_{ex} = 635 nm, 40 mW, 20 °C.

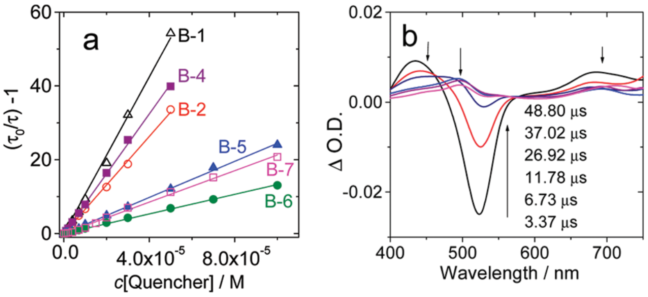


Figure 9. Stern–Volmer plots generated from triplet excited state lifetime (τ_T) quenching of compounds **B-1**, **B-2**, and **B-4** measured as a function of perylene concentration in MeCN. The quenching of **B-5**, **B-6**, and **B-7** were measured as a function of **1CBPEA** concentration in toluene. Measured with the nanosecond time-resolved transient absorption. The concentration of the sensitizers was fixed at 1.0×10^{-5} M; 20 °C. (b) Nanosecond time-resolved transient absorption difference spectra of **B-2** with 2.0×10^{-5} M of perylene added, in deaerated CH_3CN after pulsed laser excitation (λ_{ex} = 532 nm), 1.0×10^{-5} M, 20 °C.

Table 2. Triplet Excited State Lifetimes (τ_τ), Stern–Volmer Quenching Constant (K_{SV}), and Bimolecular Quenching Constants (k_q) of the BODIPY Sensitizers in Deaerated CH_3CN Solution at 20 °C

	τ_T (μs)	K_{sv} (10^3 M^{-1})	k_q (10^9 M^{-1} s^{-1})	Φ_{UC} (%)
B-1	66.3	1060.9	16.0	2.4 ± 0.0
B-2	57.1	657.7	11.5	5.4 ± 0.2
B-4	57.2	810.1	14.2	6.1 ± 0.0
B-5	54.6	244.5	4.5	0.4 ± 0.0
B-6	26.9	132.7	5.0	1.2 ± 0.1
B-7	47.0	212.9	3.8	1.7 ± 0.1

sensitizers, for which the quantum yields are known (Table 1). Upconversion in polymer films under air condition is significant because it paves the way for practical applications.[10d]

Besides the light-harvesting (ε) and ISC of the organic triplet sensitizers, TTET is another critical step involved in the cascade photophysical process of TTA UC.[8,9] TTET can be quantitatively studied by the quenching of triplet excited states of the sensitizers with perylene. Herein it was monitored by the decrease of τ_T in the presence of perylene (studied by transient absorption, Figure 9) since the T_1 states of the organic sensitizers are nonemissive. The Stern–Volmer quenching constants (K_{SV}) (Table 2) are ca. 100- to 200-fold of the reported values with transition metal complex as sensitizers,[10a,b,11a,29,30] and the bimolecular quenching constants (k_q) are among the highest values ever reported.[11a,b,29] This is attributed to the long-lived T_1 state and probably the small size of the sensitizers, with which longer diffusion distance is expected for the excited sensitizer to encounter with the acceptors.[9] Efficient TTET will improve the upconversion efficiency. The TTET was also proved by the production of the perylene T_1 state, which shows transient absorption at 495 nm (Figure 9b; note the setting of the intrument does not allow the full decay of the triplet excited state of perylene).

The upconversions are visible with the unaided eye (Figure 10). Sensitizers give green (**B-1** and **B-2**) or yellow (**B-4**) emission upon excitation at 532 nm. With addition of perylene, the fluorescence of the sensitizer and the upconverted emission of perylene were simultaneously detected (Figure 5b), the emission color changed to blue-green, blue-white, and white for **B-1**, **B-2** and **B-4**, respectively. The CIE coordinates (*x*, *y*) of the upconversion of **B-4**/perylene (0.36, 0.41) are close to the optimal white color (0.33, 0.33). We believe the color can be fine-tuned by optimization of the sensitizer/acceptor molar ratio. Previously white emission was observed with TIHF/DPA UC, but with much lower Φ_{UC} (0.6%).[27] With our iodo-BODIPY organic sensitizers the white light emission was achieved with much higher upconversion quantum yield (Φ_{UC} = 6.1%). White emission is significant because these materials can be used for energy-efficient illumination devices.

2.6. Conclusion. In summery, for the first time a series of organic triplet sensitizers (metal free) derived from a single chromophore (BODIPY) for triplet–triplet annihilation upconversion were devised, for which the absorption can be readily optimized by chemical modification of the sensitizer molecular structures. The organic sensitizers show UV–vis absorption ranging from green (510 nm) to red (629 nm) (ε is up to 180000 M^{-1} cm^{-1}) and tunable T_1 excited state energy levels. Population of the long-lived triplet excited state was observed for the organic sensitizers upon photoexcitation (τ_T is up to 66.3 μs). DFT calculations were used to rationalize the UV–vis absorption and the T_1 excited state energy levels of the sensitizers. The organic triplet sensitizers were used for triplet–triplet annihilation (TTA) based upconversion. Significant upconversion was observed in

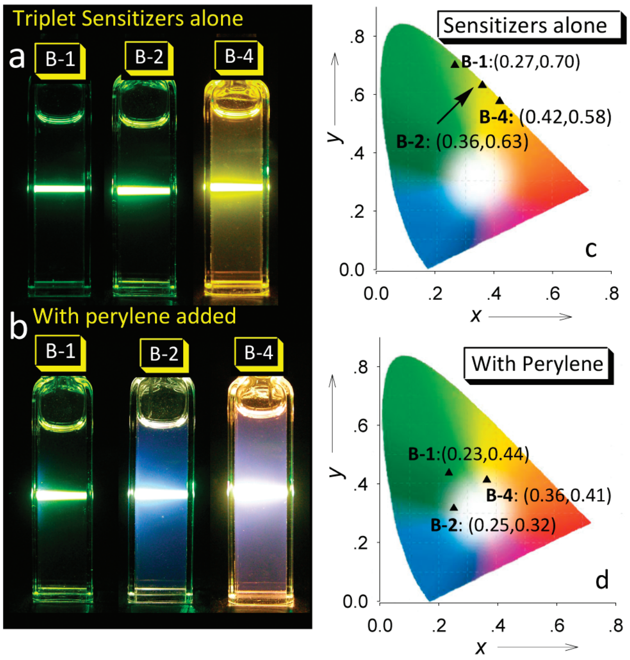


Figure 10. (a) Photographs of the emission of sensitizers alone and (b) the upconversion. (c) CIE diagram of the emission of sensitizers alone and (d) in the presence of perylene (upconversion). λ_{ex} =532 nm (5 mW); 20 °C.

solution as well as in polymer films, with quantum yield (Φ_{UC}) up to 6.1%. White light emission was observed with one of the upconversions. We believe our work will inspire the transition from metal complex sensitizers to neat organic triplet sensitizers in the research areas of TTA upconversion. This new methodology will greatly increase the availability of the triplet sensitizers that can be used for triplet—triplet annihilation based upconversion or, more generally, any other photophysical processes sensitized with triplet excited states.

3. EXPERIMENTAL SECTION

3.1. Analytical Measurements. Fluorescence lifetimes were measured with a Fluoromax-4 spectrofluorometer (Horiba Jobin Yvon). Luminescence quantum yields of the sensitizers were measured with quinine sulfate as the standard (Φ_F = 0.547 in 0.05 M sulfuric acid). All data were measured three times independently.

3.2. Synthesis of 2-Iodo-1,3,5,7-tetramethyl-8-phenyl-4,4-difluoroboradiazaindacene (B-1). At 10—15 °C, *N*-iodo-succinimid (NIS) (140.0 mg, 0.62 mmol) in anhydrous CH_2Cl_2 (10 mL) was added dropwise into a solution of **B-0** (200 mg, 0.62 mmol) in CH_2Cl_2 (50 mL) within ca. 1 h. After the addition, the reaction mixture was allowed to stir at room temperature for 1 h. The reaction mixture was then concentrated under reduced pressure, and the crude product was purified by silica gel column chromatography (hexane/CH_2Cl_2, 2:1, v/v). The second band was collected to give the product as a red solid. Yield: 191.7 mg, 68.7%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51—7.48 (m, 3H), 7.27—7.25 (m, 2H), 6.04 (s, 1H), 2.63 (s, 3H), 2.57 (s, 3H), 1.38 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.9, 154.7, 145.3, 143.4, 141.7, 135.0, 132.0, 131.1, 129.8, 129.5, 129.4, 128.0, 122.5, 84.4, 16.8, 16.0, 14.9, 14.7. MALDI-HRMS: calcd ($[C_{19}H_{18}BF_2IN_2]^+$) *m*/*z* = 450.0576, found *m*/*z* = 450.0535.

3.3. Synthesis of 2,6-Diiodo-1,3,5,7-tetramethyl-8-phenyl-4,4-difluoroboradiazaindacene (B-2).[31] To a solution of **B-0** (200 mg, 0.62 mmol) in anhydrous CH_2Cl_2 (25 mL) was added excess NIS (558 mg, 2.48 mmol). The mixture was stirred at room temperature for about 30 min (monitored by TLC until complete consumption of the starting material). The reaction mixture was then concentrated under vacuum, and the crude product was purified by silica gel column chromatography (hexane/CH_2Cl_2, 2:1, v/v). The red band was collected, and the solvent was removed under reduced pressure to give the product as red solid. Yield: 300.0 mg, 84.0%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54—7.51 (m, 3H), 7.26—7.24 (m, 2H), 2.65 (s, 6H), 1.38 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.9, 145.5, 141.5, 134.4, 129.7, 129.6, 127.9, 85.8, 17.1, 16.2. MALDI-HRMS: calcd ($[C_{19}H_{17}BF_2I_2N_2]^-$) *m*/*z* = 575.9542, found *m*/*z* = 575.9528.

3.4. Synthesis of B-3. Under nitrogen atmosphere compound **B-2** (100.0 mg, 0.174 mmol), *p*-*N*,*N*-dimethylamino-benzaldehyde (26.0 mg, 0.174 mmol), piperidine (0.1 mL), and a small amount of molecular sieves were suspended in dry toluene (20 mL). The mixture was heated to 70 °C and was kept at this temperature for about 6 h. After completion of the reaction, the majority of the solvent was evaporated under reduced pressure, and the crude product was subjected to column chromatography (silica gel, hexane/CH_2Cl_2 = 1:1) to give the product as blue solid. Yield: 40.0 mg, 32.5%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, 1H, J = 17.6 Hz), 7.59—7.50 (m, 6H), 7.28—7.27 (m, 2H), 6.81 (m, 2H), 3.06 (s, 6H), 2.68 (s, 3H), 1.44 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 151.8, 151.3, 146.6, 143.3, 140.5, 138.8, 135.3, 132.5, 131.4, 129.5, 129.4, 128.3, 124.9, 114.0, 112.2, 85.2, 82.7, 40.3, 29.7, 17.6, 16.8, 16.1. MALDI-HRMS: calcd ($[C_{28}H_{26}BF_2I_2N_3]^+$) *m*/*z* = 707.0277, found *m*/*z* = 707.0286.

3.5. Synthesis of B-4. Under argon atmosphere, 2,6-diiodo-1,3,5,7-tetramethyl-8- phenyl-4,4-difluoroboradiazaindacene (**B-2**) (150.0 mg, 0.26 mmol), $Pd(PPh_3)_2Cl_2$ (9.1 mg, 0.013 mmol), PPh_3 (6.8 mg, 0.026 mmol), and CuI (5.2 mg, 0.026 mmol) were dissolved in triethylamine (2 mL) and THF (5 mL). After stirring, trimethylsilylacetylene (25.5 mg, 0.26 mmol) was added via syringe. The solution was stirred at rt overnight. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography (silica gel, with CH_2Cl_2 as the eluent); a dark red solid was obtained. Yield: 62.2 mg, 43.8%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (m, 3H), 7.26—7.24 (m, 2H), 2.65 (s, 3H), 2.64 (s, 3H), 1.44 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 156.5, 145.3, 144.8, 142.0, 134.4, 131.8, 130.3, 129.5, 129.3, 129.3, 127.6, 116.4, 101.7, 96.9, 85.4, 16.8, 15.9, 13.6, 13.4, 0.9. MALDI-HRMS: calcd ($[C_{24}H_{26}BF_2IN_2Si]^+$) *m*/*z* = 546.0971, found *m*/*z* = 546.0938.

3.6. Synthesis of B-5. **B-5** was obtained following procedure similar to that of **B-4**, except 9-butyl-3-ethynylcarbazole (64.0 mg, 0.26 mmol) was used instead of ethynyltrimethylsilane. Yield: 30.0 mg,16.6%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21(s, 1H), 8.08 (d, 1H, J = 7.8 Hz), 7.56—7.53 (m, 4H), 7.48 (t, 1H, *J* = 7.7 Hz), 7.42 (d, 1H, *J* = 8.1 Hz), 7.35 (d, 1H, *J* = 8.5 Hz), 7.31—7.28 (m, 2H), 7.25 (d, 1H, *J* = 7.4 Hz), 4.30 (t, 2H, *J* = 7.1 Hz), 2.77 (s, 3H), 2.67 (s, 3H), 1.89—1.81 (m, 2H), 1.56 (s, 3H), 1.41 (s, 3H), 1.40—1.34 (m, 2H), 0.94 (t, 3H, *J* = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 155.9, 144.3, 144.3, 141.7, 140.9, 140.1, 134.8, 131.7, 131.0, 129.4, 129.1, 127.9, 126.1, 123.7, 122.9, 122.4, 120.5, 119.4, 117.4, 113.3, 109.0, 108.7, 98.2, 85.0, 79.4, 43.0, 31.1, 20.5, 16.8, 15.9, 13.8, 13.5. MALDI-HRMS: calcd ($[C_{37}H_{33}BF_2IN_3]^+$) *m*/*z* = 695.1780, found *m*/*z* = 695.1746.

3.7. Synthesis of a1. $Pd(PPh_3)_2Cl_2$ (29.5 mg, 0.042 mmol), PPh_3 (22.0 mg, 0.085 mmol), and CuI (17.0 mg, 0.085 mmol) were added to a solution of **B-1** (200.0 mg, 0.44 mmol) in a mixed solvent of $(i\text{-}Pr)_2NH$ (5 mL) and THF (10 mL) that had been deaerated with argon. Trimethylsilylacetylene (65.0 mg, 0.67 mmol) was added via syringe. The mixture was then heated to 60 °C for 6 h. The solvent was removed under reduced pressure, water was added, and the mixture was extracted with dichloromethane (DCM, 4 × 20 mL). The combined organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent, the crude product was purified with column chromatography (silica gel, DCM/hexane = 1:1), and a red solid was obtained. NaOH (20% in water, 0.5 mL) was added to a solution of the above trimethylsilane protected intermediate (100 mg, 0.24 mmol) in THF (4 mL) and MeOH (4 mL), and the solution was stirred at room temperature under argon for 10 min. DCM (100 mL) and water (50 mL) were added. The organic layer was separated, and the aqueous layer was extracted with DCM (3 × 15 mL). The combined organic layers were washed with brine (200 mL), dried over anhydrous $MgSO_4$, and filtered, and then the solvent was removed. The residue was purified by passing through a silica plug using DCM as eluent to give a red solid. Yield: 70.0 mg, 30.0%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52−7.49 (m, 3H), 7.28−7.25 (m, 2H), 6.04 (s, 1H), 3.28 (s, 1H), 2.64 (s, 3H), 2.57 (s, 3H), 1.44 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.3, 156.7, 145.2, 143.8, 142.5, 135.4, 134.7, 132.8, 130.0, 129.4, 128.0, 125.2, 122.5, 114.1, 83.5, 76.6, 14.9, 14.7, 13.5, 13.1.

3.8. Synthesis of a2 and a3. Under argon atmosphere, **a1** (54.2 mg, 0.16 mmol) and **B-1** (70.0 mg, 0.16 mmol) were dissolved in the mixed solvent of triethylamine (2 mL) and THF (5 mL). Then $Pd(PPh_3)_2Cl_2$ (11.0 mg, 0.016 mmol), PPh_3 (8.0 mg, 0.032 mmol), and CuI (6.2 mg, 0.032 mmol) were added, and the mixture was refluxed for about 4 h. The reaction mixture was cooled to rt, and the solvent was removed under reduced pressure. Water was added, and the mixture was extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent the crude product was purified with column chromatography (silica gel, DCM/hexane = 1:1 as eluent), and the first band was collected to give a purple solid **a2** (27.0 mg, 0.039 mmol, 49.1%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51−7.49 (m, 6H), 7.26−7.24 (m, 4H), 6.05 (s, 2H), 2.65 (s, 6H), 2.57 (s, 6H), 1.44 (s, 6H), 1.39 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 157.6, 145.4, 144.0, 142.2, 134.5, 132.9, 129.9, 127.8, 122.5, 113.7, 80.2, 75.5, 14.8, 14.6, 13.6, 13.2. MALDI-HRMS: calcd ($[C_{42}H_{36}B_2F_4N_4]^+$) m/z = 694.3062, found m/z = 694.3033. The second band was collected as a dark green solid **a3** (15.0 mg, 0.022 mmol, 13.8%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59−7.50 (m, 6H), 7.33−7.26 (m, 4H), 6.02 (s, 2H), 2.63 (s, 6H), 2.57 (s, 6H), 1.44 (s, 6H), 1.39 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.4, 156.2, 144.5, 141.9,134.7, 132.4, 132.0, 1331.7, 130.3, 129.2, 128.5, 127.9, 122.0, 120.3, 119.9, 115.7, 88.4, 88.2, 14.7, 14.5, 13.5, 13.1. MALDI-HRMS: calcd ($[C_{40}H_{36}B_2F_4N_4]^+$) m/z = 670.3062, found m/z = 670.3041.

3.9. Synthesis of B-6. **B-6** was obtained following a procedure similar to that of **B-2**, except an intermediate product **a2** (27.0 mg, 0.0403 mmol) was used instead of **B-0**; 25.7 mg of a purple solid was obtained. Yield: 67.3%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53−7.51 (m, 6H), 7.26−7.23 (m, 4H), 2.66 (s, 12H), 1.44 (s, 6H), 1.40 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 157.7, 145.9, 145.8, 142.1, 134.3, 132.3, 130.2, 129.6, 129.5, 127.7, 114.8, 86.2, 80.5, 75.4, 17.0, 16.1, 13.8, 13.5. MALDI-HRMS: calcd ($[C_{42}H_{34}B_2F_4N_4I_2]^+$) m/z = 946.0995, found m/z = 946.1037.

3.10. Synthesis of B-7. **B-7** was obtained following a similar procedure outlined above for **B-2**, except an intermediate product **a3** (10.0 mg, 0.015 mmol) was used instead of **B-0**; 7.7 mg of a blue solid was obtained, Yield: 55.7%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54−7.50 (m, 6H), 7.26−7.21 (m, 4H), 2.65 (s, 6H),2.64(s, 6H), 1.44 (s, 6H), 1.40 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.2, 156.7, 144.9, 143.8, 141.8, 134.6, 131.9, 130.7, 129.4, 127.8, 116.6, 88.7, 85., 16.9, 16.0, 13.7, 13.4. MALDI-HRMS: calcd ($[C_{40}H_{34}B_2F_4N_4I_2]^+$) m/z = 922.0995, found, m/z = 922.0933.

3.11. Nanosecond Time-Resolved Transient Difference Absorption Spectra. The nanosecond time-resolved transient absorption spectra were detected by Edinburgh analytical instruments (LP 920, Edinburgh Instruments, U.K.) and recorded on a Tektronix TDS 3012B oscilloscope. The lifetime values (by monitoring the decay trace of the transients) were obtained with the LP900 software. All samples in flash photolysis experiments were deaerated with argon for ca. 15 min before measurement, and the gas flow was maintained during the measurement.

3.12. Triplet−Triplet Annihilation Upconversions. A diode pumped solid state (DPSS) laser (532 and 635 nm) was used for the upconversions. The diameter of the 532 nm laser spot was ca. 3 mm, and for the 635 nm laser, it is ca. 6 mm. The power of the laser beam was measured with a VLP-2000 pyroelectric power meter. The samples were purged with N_2 or Ar for at least 15 min before measurement (note the upconversion can be significantly quenched by oxygen). For the upconversion experiments, the mixed solution of the BODIPYs (triplet sensitizer) and perylene or 1-chloro-bis-phenylethynylanthracene (**1CBPEA**) (triplet acceptor) was degassed for at least 15 min with N_2 or Ar. Then the solution was excited with laser. The upconverted fluorescence of perylene or **1CBPEA** was observed with spectrofluorometer. In order to suppress the laser scattering, a black box with a small hole on it was put behind the fluorescent cell to trap the laser beam (the small hole as the entrance of the laser into the black box). The polymer used for the upconversion was PEG-1500 (molecular weight 1500). The film was obtained by casting a 1.5 mL solution of PEG1500 (11% in CH_2Cl_2), to which 60 μL of sensitizer solution (1.0×10^{-3} M) and 0.7 mL of perylene solution (1.0×10^{-3} M) had been added or only 0.7 mL of perylene solution (1.0×10^{-3} M) had been added, on a glass disk. Then after evaporation of the solvents, the films were studied under air.

The upconversion quantum yields (Φ_{UC}) of **B-1**, **B-2**, and **B-4** were determined with the prompt fluorescence of the sensitizer as the inner standard; for example, Φ_{UC} of **B-2** was determined by comparing the upconverted fluorescence and its prompt fluorescence. For **B-5**, **B-6**, and **B-7**, Φ_{UC} was determined with the prompt fluorescence of **B-5** as the standard. The upconversion quantum yields were calculated with the following equation, where Φ_{UC}, A_{unk}, I_{unk}, and η_{unk} represent the quantum yield, absorbance, integrated photoluminescence intensity, and the refractive index of the solvents (eq 1). The equation is multiplied by a factor of 2 in order to make the maximum quantum yield to be unity.[10c] All these data were independently measured three times (with different solutions samples).

$$\Phi_{UC} = 2\Phi_{std}\left(\frac{A_{std}}{A_{unk}}\right)\left(\frac{I_{unk}}{I_{std}}\right)\left(\frac{\eta_{unk}}{\eta_{std}}\right)^2 \qquad (1)$$

For the measurement of the TTET efficiency, i.e., the Stern−Volmer quenching constants, the concentration of the sensitizer was fixed at 1.0×10^{-5} M, and the lifetime of the sensitizer was measured with increasing perylene concentration in the solution.

The CIE coordinates (x, y) of the emission of the sensitizers alone and the emission of the upconversion were derived from the emission spectra with CIE Color Matching Linear Algebra software.

3.13. DFT Calculations. The density functional theory (DFT) calculations were used for optimization of the ground state geometries of both singlet states and triplet states. The energy level of the T_1 state (energy gap between S_0 state and T_1 state) were calculated with time-dependent DFT (TDDFT), based on the optimized singlet ground state geometries (S_0 state). TDDFT calculations were also used for the prediction of the UV−vis absorption of the organic triplet sensitizers at triplet state, and in our case it is the transient absorption of the organic triplet sensitizers after laser flash (the pulsed excitation of the organic triplet sensitizer solution). Please note that the bleaching bands in the time-resolved transient absorption spectra cannot be predicted by the TDDFT calculations. All the calculations were performed with Gaussian 09W.[32]

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Synthesis of **B-0** and the structure characterization data of the organic triplet sensitizers, details of upconversion, transient absorption, calculation information, 77 K emission spectra, and photostability of the sensitizers and photophysics of the acceptors. This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES

(1) Baluschev, S.; Yakutkin, V.; Miteva, T.; Avlasevich, Y.; Chernov, S.; Aleshchenkov, S.; Nelles, G.; Cheprakov, A.; Yasuda, A.; Müllen, K.; Wegner, G. *Angew. Chem., Int. Ed.* **2007**, *46*, 7693–7696.

(2) Warther, D.; Bolze, F.; Léonard, J.; Gug, S.; Specht, A.; Puliti, D.; Sun, X. H.; Kessler, P.; Lutz, Y.; Vonesch, J. L.; Winsor, B.; Nicoud, J. F.; Goeldner, M. *J. Am. Chem. Soc.* **2010**, *132*, 2585–2590.

(3) Zhang, P.; Wang, M.; Dong, J.; Li, X.; Wang, F.; Wu, L.; Sun, L. *J. Phys. Chem. C* **2010**, *114*, 15868–15874.

(4) Kim, H. M.; Cho, B. R. *Acc. Chem. Res.* **2009**, *42*, 863–872.

(5) Kim, M. K.; Lim, C. S.; Hong, J. T.; Han, J. H.; Jang, H. Y.; Kim, H. M.; Cho, B. R. *Angew. Chem., Int. Ed.* **2010**, *49*, 364–367.

(6) Kushwaha, S. K.; Shakir, M.; Maurya, K. K.; Shah, A. L.; Wahab, M. A.; Bhagavannarayana, G. *J. Appl. Phys.* **2010**, *108*, 033506/1–033506/7.

(7) Tian, H.; Jiang, X.; Yu, Z.; Kloo, L.; Hagfeldt, A.; Sun, L. *Angew. Chem.* **2010**, *122*, 7486–7489; *Angew. Chem., Int. Ed.* **2010***49*, 7328−7331.

(8) Matsunami, M.; Chainani, A.; Taguchi, M.; Eguchi, R.; Ishida, Y.; Takata, Y.; Okamura, H.; Nanba, T.; Yabashi, M.; Tamasaku, K.; Nishino, Y.; Ishikawa, T.; Senba, Y.; Ohashi, H.; Tsujii, N.; Ochiai, A.; Shin, S. *Phys. Rev. B* **2008**, *78*, 195112/1–195112/5.

(9) (a) Parker, C. A.; hatchard, C. G.; Joyce, T. A. *Nature* **1965**, *205*, 1282–1284. (b) Monguzzi, A.; Tubino, R.; Meinardi, F. *Phys. Rev. B* **2008**, *77*, 155122/1–155122/4.

(10) (a) Islangulov, R. R.; Kozlov, D. V.; Castellano, F. N. *Chem. Commun.* **2005**, 3776–3778. (b) Singh-Rachford, T. N.; Islangulov, R. R.; Castellano, F. N. J. *Phys. Chem. A* **2008**, *112*, 3906–3910. (c) Singh- Rachford, T. N.; Castellano, F. N. *Coord. Chem. Rev.* **2010**, *254*, 2560–2573. (d) Islangulov, R. R.; Lott, J.; Weder, C.; Castellano., F. N. *J. Am. Chem. Soc.* **2007**, *129*, 12652–12653.

(11) (a) Singh-Rachford, T. N.; Castellano, F. N. *J. Phys. Chem. Lett.* **2010**, *1*, 195–200. (b) Cheng, Y. Y.; Fückel, B.; Khoury, T.; Clady, R. G. C. R.; Tayebjee, M. J. Y.; Ekins-Daukes, N. J.; Crossley, M. J.; Schmidt, T. W. *J. Phys. Chem. Lett.* **2010**, *1*, 1795–1799.

(12) (a) Kozlov, D. V.; Castellano, F. N. *Chem. Commun.* **2004**, 2860–2861. (b) Ji, S.; Wu, W.; Wu, W.; Guo, H.; Zhao, J. *Angew. Chem., Int. Ed.* **2011**, *50*, 1626–1629.(c) Ji, S.; Guo, H.; Wu, W.; Wu, W. Zhao, J. *Angew. Chem., Int. Ed.* **2011**; Epub ahead of print, DOI: 10.1002/anie.201008134. (d) Wu, W.; Wu, W.; Ji, S.; Guo, H.; Zhao, J. *Dalton Trans.* **2011**, *40*, 5953–5963.(d) Liu, Y.; Wu, W.; Zhang, X.; Guo, H.; Zhao, J. *Dalton Trans.* **2011**; Epub ahead of print, DOI: 10.1039/c1dt10679a. (e) Sun, H.; Guo, H.; Wu, W.; Liu, X.; Zhao, J. *Dalton Trans.* **2011**, *40*, 7834−7841. (f) Sun, J.; Wu, W.; Guo, H.; Zhao, J. *Eur. J. Inorg. Chem.* **2011**, 3165−3173.

(13) Singh-Rachford, T. N.; Castellano, F. N. *Inorg. Chem.* **2009**, *48*, 2541–2548.

(14) Singh-Rachford, T. N.; Castellano, F. N. *J. Phys. Chem. A* **2008**, *112*, 3550–3556.

(15) Wolfbeis, O.; Narayanaswamy, R. *Optical Sensors: Industrial, Environmental and Diagnostic Applications*; Springer-Verlag: Berlin, Heidelberg, 2004.

(16) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*, 2nd ed.; Kluwer Academic: New York, 1999.

(17) Yogo, T.; Urano, Y.; Ishitsuka, Y.; Maniwa, F.; Nagano, T. *J. Am. Chem. Soc.* **2005**, *127*, 12162–12163.

(18) Gorman, A.; Killoran, J.; O'Shea, C.; Kenna, T.; Gallagher, W. M.; O'Shea, D. F. *J. Am. Chem. Soc.* **2004**, *126*, 10619–10631.

(19) (a) Ulrich, G.; Ziessel, R.; Harriman, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 1184–1201. (b) Zhang, X.; Xiao, Y.; Qian, X. *Angew. Chem., Int. Ed.* **2008**, *47*, 8025–8029. (c) Peng, X.; Du, J.; Fan, J.; Wang, J.; Wu, Y.; Zhao, J.; Sun, S.; Xu., T. *J. Am. Chem. Soc.* **2007**, *129*, 1500–1501. (d) Ziessel, R.; Harriman, A. *Chem. Commun.* **2011**, *47*, 611–631. (e) Guliyev, R.; Coskun, A.; Akkaya., E. U. *J. Am. Chem. Soc.* **2009**, *131*, 9007–9013.

(20) Lee, J. S.; Kang, N. Y.; Kim, Y. K.; Samanta, A.; Feng, S.; Kim, H. K.; Vendrell, M.; Park, J. H.; Chang, Y. T. *J. Am. Chem. Soc.* **2009**, *131*, 10077–10082.

(21) Singh-Rachford, T. N.; Haefele, A.; Ziessel, R.; Castellano, F. N. *J. Am. Chem. Soc.* **2008**, *130*, 16164–16165.

(22) (a) Baruah, M.; Qin, W.; Flors, C.; Hofkens, J.; Vallée, R. A. L.; Beljonne, D.; der Auweraer, M. V.; De Borggraeve, W. M.; Boens, N. *J. Phys. Chem. A* **2006**, *110*, 5998–6009.(b) Turro, N. J.; Ramamurthy, V.; Scaiano, J. C. *Principles of Molecular Photochemistry: An Introduction*; University Science Books: Sausalito, CA, 2009. (c) Immitzer, B.; Falk, H. *Monatsh. Chem.* **2000**, *131*, 1167–1171.

(23) Galletta, M.; Campagna, S.; Quesada, M.; Ulrich, G.; Ziessel, R. *Chem. Commun.* **2005**, 4222–4224.

(24) Rachford, A. A.; Ziessel, R.; Bura, T.; Retailleau, P.; Castellano, F. N. *Inorg. Chem.* **2010**, *49*, 3730–3736.

(25) (a) Galletta, M.; Puntoriero, F.; Campagna, S.; Chiorboli, C.; Quesada, M.; Goeb, S.; Ziessel, R. *J. Phys. Chem. A* **2006**, *110*, 4348–4358.

(26) Singh-Rachford, T. N.; Castellano, F. N. *J. Phys. Chem. A* **2009**, *113*, 5912–5917.

(27) Chen, H. C.; Hung, C. Y.; Wang, K. H.; Chen, H. L.; Fann, W. S.; Chien, F. C.; Chen, P.; Chow, T. J.; Hsu, C. P.; Sun, S. S. *Chem. Commun.* **2009**, 4064–4066.

(28) Cheng, Y. Y.; Khoury, T.; Clady, R. G. C. R.; Tayebjee, M. J. Y.; Ekins-Daukes, N. J.; Crossleya, M. J.; Schmidt, T. W. *Phys. Chem. Chem. Phys.* **2010**, *12*, 66–71.

(29) Du, P.; Eisenberg, R. *Chem. Sci.* **2010**, *1*, 502–506.

(30) Zhao, W.; Castellano, F. N. *J. Phys. Chem. A* **2006**, *110*, 11440–11445.

(31) Zhang, D.; Wang, Y.; Xiao, Y.; Qian, S.; Qian, X. *Tetrahedron* **2009**, *65*, 8099–8013.

(32) Frisch, M. J. et al. *Gaussian 09 Revision A.1*; Gaussian Inc.: Wallingford, CT, 2009.