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Room-Temperature Long-Lived Triplet Excited States of Naphthalenediimides and Their Applications as Organic Triplet Photosensitizers for Photooxidation and Triplet–Triplet Annihilation Upconversions

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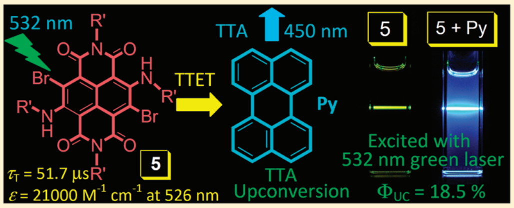
Supporting Information

ABSTRACT: Naphthalenediimide (NDI) derivatives with 2,6- or 2,3,6,7-tetrabromo or amino substituents were prepared. *N,N′*-dialkyl-2,6-dibromo NDI (compound **2**) and *N,N′*-dialkyl-2,3,6,7-tetrabromo NDI (compound **4**) show phosphorescence emission at 610 or 667 nm, respectively. Phosphorescence was never observed for NDI derivatives. Conversely, *N,N′*-dialkyl-2,6-dibromo-3,7-diamino NDI (compound **5**) shows strong absorption at 526 nm and fluorescence at 551 nm, and no phosphorescence was observed. However, nanosecond time-resolved transient difference absorption spectroscopy confirmed that the triplet excited state of **5** was populated upon photoexcitation. 2,3,6,7-Tetraamino NDI (**6**) shows fluorescence, and no triplet excited state was populated upon excitation. The compounds were used as singlet oxygen ($^1O_2$) photosensitizers for the photooxidation of 1,5-dihydroxylnaphthalene (DHN). We found that **5** is more efficient than the conventional photosensitizer, such as Ir(ppy)$_2$(bpy)[PF$_6$]. The compounds were also used as organic triplet photosensitizers for triplet–triplet annihilation based upconversions. An upconversion quantum yield up to 18.5% was observed.



1. INTRODUCTION

Triplet photosensitizers have attracted much attention due to the applications for singlet oxygen production, such as photodynamic therapy (PTD),[1−4] photocatalysis,[5] upconversions, etc.[6−9] The triplet sensitizers used for these photophysical processes are usually limited to the phosphorescent transition-metal complexes, such as Pt(II)/Pd(II) porphyrin complexes, Ru(II) polyimine complexes, or the Ir(III)/Pt(II) complexes, etc., because the intersystem crossing process (ISC) of these compounds is efficient due to the heavy atom effect of the transition-metal atoms. However, these conventional transition-metal complex photosensitizers suffer from some disadvantages, such as weak absorption of visible light and the short-lived triplet excited states. Development of *organic* triplet sensitizers that show *strong* absorption of visible light and a *long-lived* T_1 excited state are highly desired. Recently boron-dipyrromethene (BODIPY)-based triplet sensitizers have been developed for PDT and triplet–triplet annihilation (TTA) upconversions.[2,9,10] However, much room is left for development of an organic triplet sensitizer with chromophores other than the BODIPY moiety. For example, a TTA upconversion quantum yield of 6.1% was observed with iodo-BODIPY organic triplet photosensitizers.[9] New organic triplet photosensitizers with a *higher* TTA upconversion quantum yield are desired.[7a]

Concerning this aspect, naphthalenediimide (NDI) has attracted much attention, due to the applications in fluorescent dyes, molecular probes, supramolecular assemblies, photoinduced charge transfer, etc.[11−19] The fluorescence of NDI derivatives has been studied in detail. NDIs, especially those with amino substituents, show strong absorption of visible light and intense emission in the red range.[13] Recently, we studied the NDI-containing Pt(II) complex, and the room-temperature (RT) phosphorescence of the NDI ligand was observed.[20] Previously, the triplet excited state of the organic NDI chromophore was reported, but the excitation was at the UV range (<400 nm), and no RT phosphorescence was observed.[14,18,21] No NDI-based triplet photosensitizers have been reported.

To prepare organic triplet photosensitizers that show strong absorption of visible light and long-lived triplet excited states, inspired by the previous study of NDI,[11,13,15,17] herein, we used the NDI core to prepare the desired triplet photosensitizers (Scheme 1). With di- and tetrabromination, phosphorescence was observed for the NDI derivatives. Long-lived triplet excited states were observed for all the bromo-containing derivatives. The NDI derivatives were used as triplet sensitizers for photooxidation (via sensitizing singlet oxygen), as well as TTA-based upconversions.

2. RESULTS AND DISCUSSION

2.1. Synthesis of the NDI-Based Organic Triplet Sensitizers. The synthesis of the NDI derivatives is outlined

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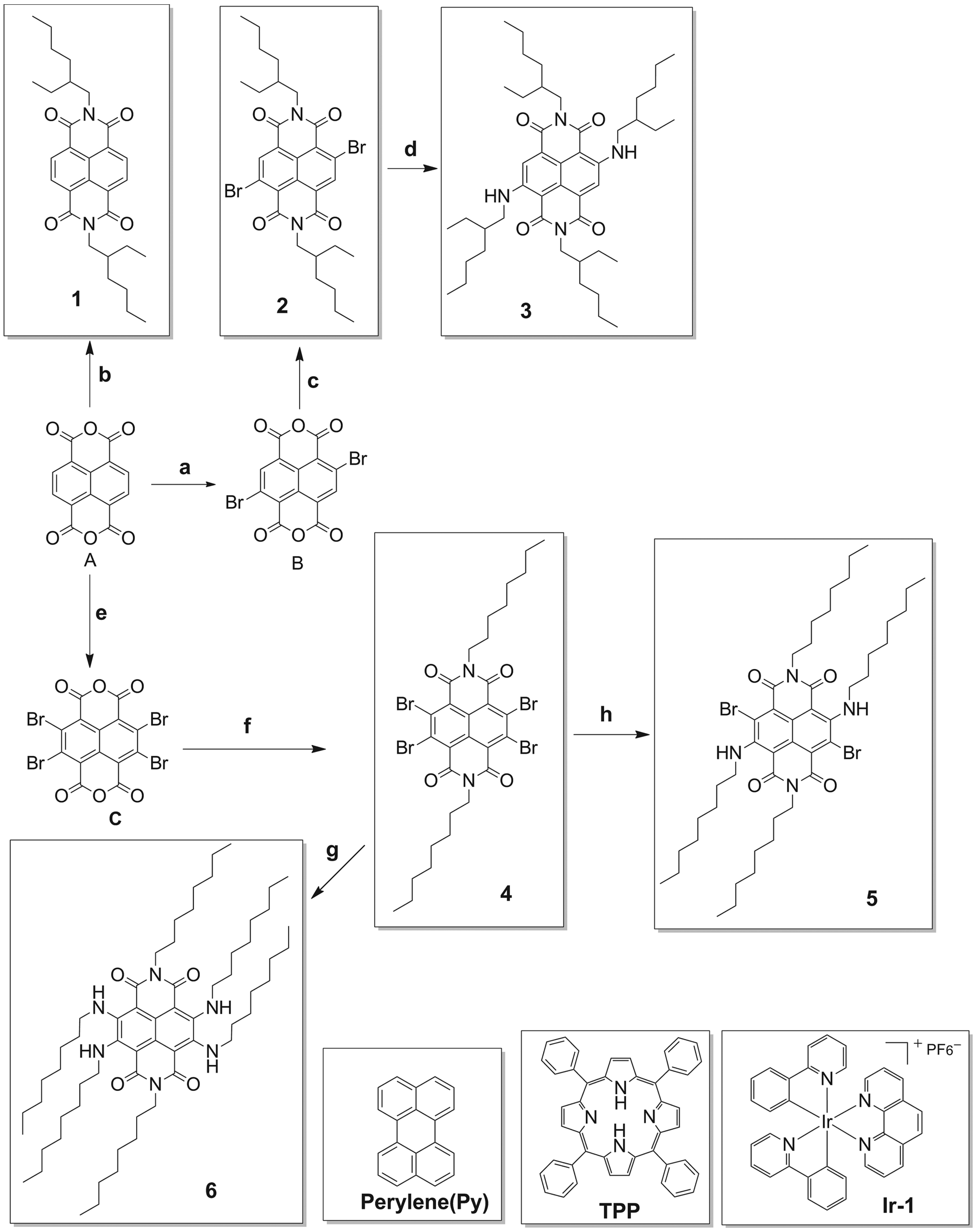
Scheme 1. Synthesis of the Naphthalenediimide (NDI) Derivatives 1−6. The Triplet Acceptor Perylene and the Model Triplet Sensitizers Tetraphenylporphyrin (TPP) and Ir(ppy)$_2$(phen)[PF$_6$] (Ir-1) Are Also Presented[a]



[a] (a) Dibromoisocyanuric acid (DBI), oleum (20% SO$_3$), 40 °C, 5 h; yield: 83%; (b) 2-ethylhexylamine, freshly distilled DMF, under N$_2$, 140 °C, overnight; yield: 56%; (c) 2-ethylhexylamine, 120 °C, under N$_2$, 2 h; yield: 35%; (d) 2-ethylhexylamine, 140 °C, under Ar, 2 h; yield: 45%; (e) DBI, oleum (20% SO$_3$), 25 °C, 3 h; yield: 93%; (f) *n*-octylamine, acetic acid, 90 °C, 30 min, under N$_2$; PBr$_3$, dry toluene, reflux, 12 h, under N$_2$; yield: 43%; (g) *n*-octylamine, dry DMF, 135 °C, 6 h; yield: 33%; (h) *n*-octylamine, dry DMF, 135 °C, 6 h; yield: 44%.

in Scheme 1. The synthetic strategy used was similar to the previously reported methods by Würthner and Matile, etc.[11−13] Bromination of the naphthalenedianhydride gives the 2,6-bis-bromo anhydride (**B**). Reaction with alkylamine leads to the bisamide **2**. We envisaged that compound **2** may show a triplet excited state, due to the heavy atom effect of the bromo substituents. The heavy atom effect can be maximized in compound **4**, in which four bromo atoms are attached to the NDI core. However, both compound **2** and compound **4** show absorption in the UV range. To obtain triplet photosensitizer showing absorption in the red shifted range,[21] we devised compound **5**. The two bromo atoms in compound **5** may exert the heavy atom effect, whereas the amino substituent will move the absorption into the visible range.[13,17a] Previously, the triplet state of NDI was observed, but the absorption was in the UV range.[21] To access the compounds that show red shifted absorption, compounds **3** and **6** were prepared. **1** was used as a model compound for the photophysical studies. All the compounds were obtained in satisfying yields.

2.2. UV−vis Absorption and Fluorescence Spectra of the Compounds. The UV−vis absorption spectra of the NDI derivatives were studied (Figure 1). The naphthalenediimide (**1**) shows absorption in the UV range (386 nm, ε = 16 000 M^{-1} cm^{-1}). After bromination, the absorption is red shifted to 410 nm (compound **2**, Figure 1a). With amino substitution of the bromo substituents, the absorption maxima is red shifted to 617 nm (compound **3**, ε = 9000 M^{-1} cm^{-1}). Thus, the effect of amino substitution on the UV−vis absorption of the NDI derivatives is significant. The absorption wavelength of **3** is in full agreement with a previous study of the compound.[11a]

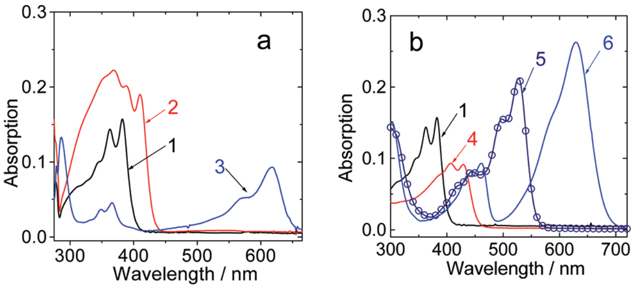


Figure 1. UV−vis absorption of compounds (a) **1**−**3**, and (b) **1** and **4**−**6**; 1.0 × 10^{-5} M in toluene, 20 °C.

Tetrabromo NDI (**4**) shows red shifted absorption compared with that of compound **1** (Figure 1b). Absorption maxima at 428 and 406 nm were observed for **4**, which is in agreement with the previous study.[12a] With bisamino substitution, the absorption of compound **5** is red shifted to 526 nm (ε = 21 000 M^{-1} cm^{-1}). However, the absorption of **5** is significantly blue shifted compared with the absorption of compound **3** (617 nm). NDI with four amino substituents (**6**) shows an intense absorption at 629 nm (ε = 26 000 M^{-1} cm^{-1}) (Figure 1b). These results show that the UV−vis absorption of the NDI derivatives can be readily tuned by increasing the amino substituents on the NDI core.

The RT luminescence of the NDI derivatives in fluid solution was studied (Figure 2). Derivatives with amino substituents, such as compounds **3** and **6**, give an intense emission at 645 nm (Φ_F = 61.1%) and 668 nm (Φ_F = 16.2%), respectively. The fluorescence properties of these two compounds are similar to the compounds reported by Würthner et al.[11a,13] The unsubstituted naphthalenediimide (**1**) gives a weak emission at a much shorter wavelength (386 nm, Φ_F = 0.95%). Compounds **2** and **4** are nonluminescent in aerated solution. Interestingly, both compounds give a strong emission in deaerated solution at 610 and 667 nm, respectively (Figure 2b,d). The emissive wavelengths are close to the phosphorescence emission of NDI.[21a] Thus, we propose that the emission observed for compounds **2** and **4** is phosphorescence and is fluorescence for compounds **1**, **3**, **5**, and **6**. Previously, the dibromo or tetrabromo NDI was prepared, but all those compounds were found to be nonfluorescent.[11a,13,14a] The phosphorescence of **2** and **4** was confirmed by the quenched emission in aerated solution. To the best of our knowledge, this is the first time that the phosphorescence was observed for the NDI chromophore, without the heavy atom effect of transition-metal atoms.[20] Previously, phosphorescence was observed for NDI derivatives only at 77 K and with an external heavy atom effect.[21a,c] 2,6-Dibromo NDI has been reported, but no phosphorescence was reported.[17] 2,3,6,7-Tetrabromo NDI was also reported, however, the photophysical properties and the RT phosphorescence property were not studied.[12,13] Recently, we prepared iodo-substituted BODIPY based organic triplet sensitizers, but no RT phosphorescence was observed.[9]

The photophysical parameters of the compounds are compiled in Table 1. The compounds **1**, **3**, **5**, and **6** give luminescence lifetimes in the nanosecond range, which are in agreement with the fluorescence feature of the emission of these compounds. The fluorescence lifetime of compound **5** is much shorter (0.08 ns). Instead, triplet excited states with much longer lifetimes were observed for compounds **2**, **4**, and **5** (see later section for details). We noticed that compound **5** shows a much weaker emission than compound **3** and compound **6**. We propose that ISC is significant for **5**, due to the presence of bromo substituents in this compound.

The red shifted absorption of the amino-substituted compounds may be due to the elevated energy level of the

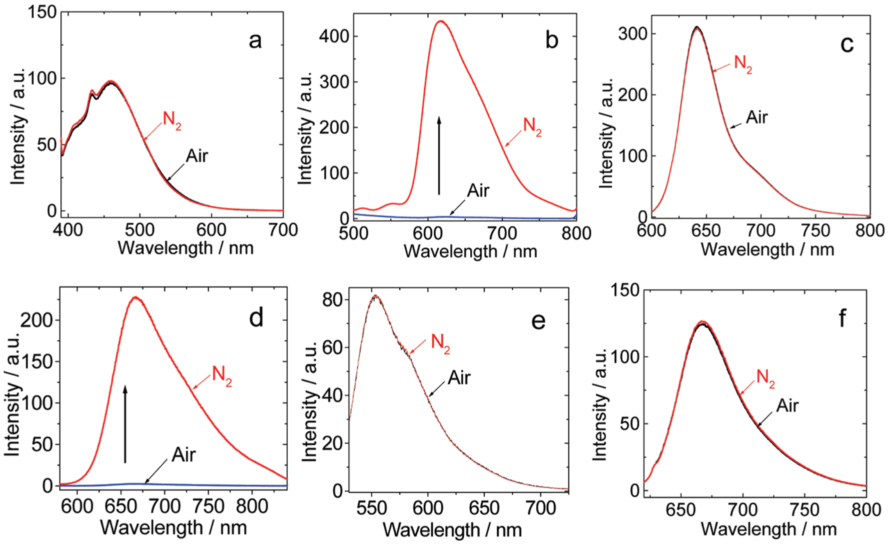


Figure 2. Emission spectra of compounds under nitrogen and air atmospheres: (a) compound **1**, λ_{ex} = 378 nm; (b) **2**, λ_{ex} = 350 nm; (c) **3**, λ_{ex} = 590 nm; (d) **4**, λ_{ex} = 429 nm; (e) **5**, λ_{ex} = 490 nm; (f) **6**, λ_{ex} = 629 nm; 1.0 × 10^{-5} M in toluene, 20 °C.

Table 1. Photophysical Parameters of the Compounds

	λ_{abs}[a]	ε[b]	λ_{em}[a]	Φ_F (%)[c]	Φ_P (%)[d]	τ_F/ns[e]	τ_T/μs[f]	$\Delta E/T_1-S_0$[g]
1	362, 386	0.14, 0.16	470	0.95 ± 0.1	h	2.11	h	h
2	368, 410	0.22, 0.19	610	h	0.12 ± 0.01	h	6.1	2.06
3	617	0.09	645	61.1 ± 0.3	h	9.70	h	h
4	406, 428	0.09, 0.09	667	h	0.13 ± 0.01	h	11.1	2.00
5	526, 496	0.21, 0.15	551	0.2 ± 0.1	h	0.08	51.7	h
6	629	0.26	668	16.2 ± 0.3	h	4.37	h	h

[a] In toluene (1.0×10^{-5} M); in nm. [b] Molar extinction coefficient; 10^5 M^{-1} cm^{-1}. [c] Fluorescence quantum yields. Determined with quinine sulfate ($\Phi_F = 0.547$ in 0.05 M sulfuric acid) and BODIPY ($\Phi_F = 0.72$ in THF) as standard. In toluene. [d] Phosphorescence quantum yields. Determined with $Ru(Phen)(bpy)_2[PF_6]_2$ as the standard ($\Phi_P = 0.060$ in acetonitrile). In toluene. [e] Fluorescence lifetimes. [f] Triplet state lifetimes, measured by transient absorption. 3.0×10^{-5} M in toluene. [g] The calculated energy gap between S_0 and T_1 states (TDDFT); in eV. [h] Not applicable.

Table 2. Energy Level of the HOMO and LUMO Orbitals and the HOMO−LUMO Energy Gap ($\Delta E_{HOMO-LUMO}$) of Compounds 1−6 (in eV)[a]

	1	2	3	4	5	6
HOMO	−6.96	−7.01	−5.48	−6.52	−5.57	−5.07
LUMO	−3.34	−3.54	−2.74	−3.64	−2.92	−2.47
$\Delta E_{HOMO-LUMO}$	3.62	3.47	2.74	2.88	2.65	2.60

[a] Based on optimized ground state geometries (DFT//B3LYP/6-31G(d)). Toluene was used as solvent in the calculation.

HOMO orbitals of the compounds, thus the smaller energy gap between the HOMO and LUMO orbitals (Table 2).

2.3. Nanosecond Time-Resolved Transient Difference Absorption Spectroscopy. The population of the triplet excited states of the compounds upon photoexcitation can be studied by the nanosecond time-resolved transient difference absorption spectroscopy (Figure 3).

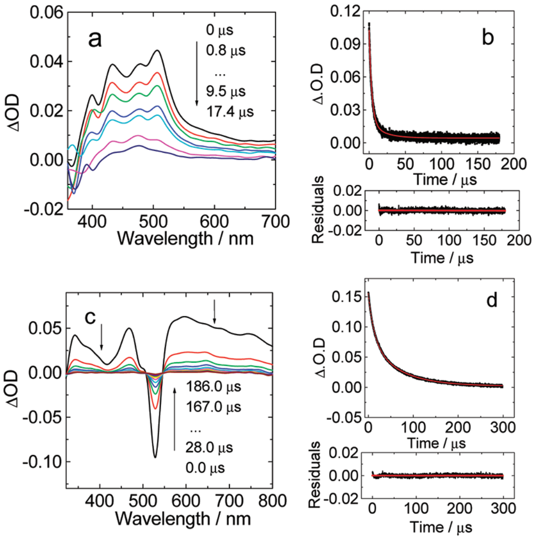


Figure 3. Nanosecond time-resolved transient difference absorption spectra of compounds **2** and **5**. Transient absorption with different delay times: (a) compound **2** (λ_{ex} = 355 nm), (c) compound **5** (λ_{ex} = 532 nm). (b) Decay trace of **2** at 530 nm (λ_{ex} = 355 nm). (d) Decay trace of **5** at 530 nm (λ_{ex} = 532 nm); 3.0×10^{-5} M in toluene after pulsed laser excitation under N_2 atmosphere, 20 °C.

Upon pulsed laser excitation at 355 nm, transient absorption in the range of 400−600 nm developed for compound **2**. The lifetime of this transient band is 6.1 μs. In aerated solution, the lifetime of this transient is greatly reduced (0.6 μs). Thus, this oxygen sensitivity of the transient species of **2** upon pulsed laser excitation confirms the triplet feature of the excited state of compound **2**.

Compound **5** shows fluorescence, and no phosphorescence was observed at RT (Figure 2). However, this result does not necessarily mean that the triplet excited state of compound **5** is not populated upon photoexcitation.[9] Upon pulsed laser excitation at 532 nm, significant bleaching was observed at 528 nm. At the same time, transient absorption bands at 339 and 469 nm and in the range of 550−800 nm were observed. The bleaching at 528 nm is due to the depletion of the ground state of the compounds upon population of the triplet excited state. Transient absorption bands at 339 nm and in the range of 450−800 nm are due to the transient absorption of the T_1 excited state of compound **5**.[21] The triplet feature of the excited state of compound **5** was confirmed by the sensitivity to O_2. The lifetime of the transients of **5** was determined as 51.7 μs in *deaerated* solution. The lifetime of the long-lived triplet excited state is comparable to the triplet excited state of the BODIPY-based triplet photosensitizer.[9] In *aerated* solution, however, the lifetime of the transients was reduced to less than 0.01 μs. Previously, the triplet excited states of NDI derivatives have been observed, but the absorption of these compounds is in the UV range.[21] The visible light excitable compound **5** is significant for application of these sensitizers.

These results indicate that the long-lived triplet excited states of the compounds were populated upon visible light excitation. Such organic triplet sensitizers with visible light-harvesting capability can be used for a wide variety of photophysical processes that involve triplet−triplet energy transfer (TTET), such as singlet oxygen sensitizing and TTA upconversion.[5−9]

No long-lived transients were observed for compound **6**. The lack of the long-lived transient species demonstrated the elusive photophysical properties, despite the presence of the four carbonyl groups in compound **6**.[21]

2.4. DFT Calculations on the Photophysical Properties of the NDI Derivatives. Photophysical properties of the fluorophores and molecular probes have been studied with DFT computations, in most cases, with the consideration of frontier molecular orbitals, such as HOMO and LUMO. Recently, we and others proposed that the photophysical properties of the fluorophores can be studied with the consideration of *electronic excited states*, instead of the

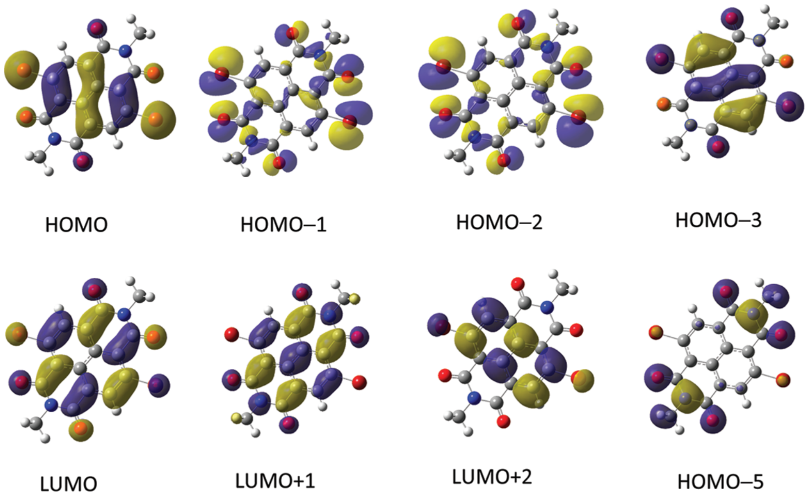


Figure 4. Frontier molecular orbitals of compound **2** based on the optimized ground-state geometry. Toluene was used as the solvent in the calculations (PCM model). Calculated at the B3LYP/6-31g(d) level with Gaussian 09W. Please note that the alkyl chains were simplified as methyl groups in order to reduce the computation time.

approximation with the concept of *molecular orbitals*.[22,23] Herein, the UV−vis absorption and the emission of the compounds were studied with the DFT calculations. (The results of compound **2** are presented in Figure 4 and Table 3. For the results of the other compounds, please refer to the Supporting Information.) The DFT calculations predict that the absorption band is at 403 nm, which is in good agreement with the experimental result (410 nm, Figure 1). The calculation also predicted absorption at 361 nm, which is in good agreement with the experimental results (Figure 1).

Table 3. Electronic Excitation Energies (eV) and Corresponding Oscillator Strengths (*f*), Main Configurations, and CI Coefficients of the Low-Lying Electronically Excited States of 2, Calculated by TDDFT//B3LYP/6-31G(d), Based on the Optimized Ground-State Geometries[f]

		TDDFT//B3LYP/6-31G(d)			
	electronic transition	energy[a]	*f*[b]	composition[c]	CI[d]
singlet	$S_0 \to S_1$	2.94 eV/ 422 nm	0.0000	HOMO−1 → LUMO	0.6956
	$S_0 \to S_2$	2.97 eV/ 418 nm	0.0002	HOMO−2 → LUMO	0.6956
	$S_0 \to S_3$	3.07 eV/ 403 nm	0.2361	HOMO−3 → LUMO	0.1413
				HOMO → LUMO	0.6845
	$S_0 \to S_4$	3.43 eV/ 361 nm	0.2668	HOMO−3 → LUMO	0.6723
				HOMO → LUMO	0.1523
				HOMO → LUMO+2	0.1101
	$S_0 \to S_8$	3.83 eV/ 324 nm	0.1518	HOMO−5 → LUMO	0.6931
singlet[e]	$S_1 \to S_0$[e]	1.54 eV/ 807 nm	0.0000	HOMO → LUMO	0.6998
triplet	$S_0 \to T_1$	2.06 eV/ 602 nm	0.0000	HOMO−3 → LUMO	0.3001
				HOMO → LUMO	0.6201

[a] Only the selected low-lying excited states are presented. [b] Oscillator strength. No spin−orbital coupling effect was considered in the calculation; thus, the oscillators are zero. [c] Only the main configurations are presented. [d] The CI coefficients are in absolute values. [e] Emission. Note that the calculation of the emission by TDDFT methods gives the information for the $S_0 \to S_1$ transition. [f] Toluene was used as solvent in the calculation.

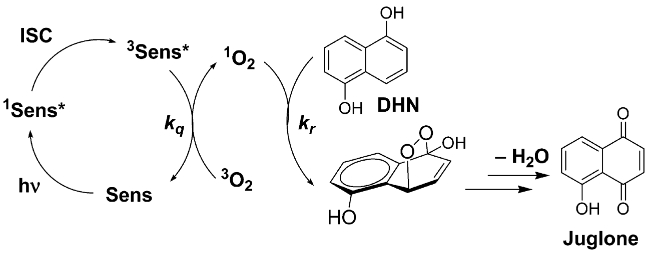
The calculations predicted a forbidden transition of $S_0 \to S_1$, as well as $S_0 \to S_2$ (Table 3). On the basis of the molecular orbitals involved in the transitions (Table 3), the HOMO−1 and LUMO are involved in the $S_0 \to S_1$ transition. There is no overlap for the HOMO−1 and LUMO electron distributions. For the allowed transitions, such as $S_0 \to S_3$ (excitation energy, 403 nm), the MOs involved in the transition are HOMO and LUMO; these MOs show overlap, which is a typical feature for the allowed transition.

The emissions of compound **2** were also studied with the time-dependent DFT (TDDFT) (Table 3), based on the optimized S_1 state geometry (under these circumstances, the calculated energy gap between the S_1 and S_0 states is the fluorescence emission). According to Kasha's rule, the S_1 excited state is usually responsible for the fluorescence emission of the fluorophore. The calculated emission wavelength is at 807 nm, with an oscillator strength of zero. The oscillator strength indicated that $S_1 \to S_0$ is a forbidden transition, and no fluorescence will be observed. This is in agreement with the experimental results that no fluorescence was observed for compound **2**. The TDDFT calculations predicted that the phosphorescence band is at 602 nm, which is in good agreement with the experimental result at 610 nm (Figure 2b and Table 3). Similar calculations were carried out for other compounds (see the Supporting Information).

2.5. Application of the Organic Triplet Sensitizers for Photooxidation of 1,5-Dihydroxylnaphthalene (DHN).

Recently, cyclometalated Ir(III) complexes, such as Ir(ppy)$_3$ (where ppy = 2-phenylpyridine), were used as a triplet sensitizer for hydrogen production by photocatalytic splitting of water, or as the singlet oxygen photosensitizer for photooxidation of 1,5-dihydronaphthalene (DHN) (Scheme 1).[5,24] However, these Ir(III) complexes show very weak absorption of visible light and the T_1 excited state of these complexes have short lifetimes (less than 5 μs). Furthermore, organic triplet photosensitizers are more cost-efficient. Thus, we propose to use the NDI compounds (Scheme 2) as triplet

Scheme 2. Mechanism for the Photooxidation of DHN with Singlet Oxygen ($^1O_2$) Photosensitizer



sensitizers for these purposes. As a proof-of-concept, we studied the application of the compounds as triplet photosensitizers (singlet oxygen sensitizer) in the photooxidation of DHN.

The photooxidation of DHN with the triplet sensitizer can be illustrated in Scheme 2.[5] Upon photoexcitation, the singlet oxygen ($^1O_2$) will be produced with the sensitization of the $^3O_2$ by the triplet sensitizer. The DHN can then be oxidized by the $^1O_2$. The process can be followed by monitoring the UV−vis absorption changes at 301 nm (decreased absorption, due to consumption of DHN by $^1O_2$). Sensitizers with strong absorption of visible light and a long-lived T_1 excited state are ideal for the sensitizing of $^1O_2$; the process can be described as TTET. It should be pointed out that the NDI derivatives we developed (Scheme 1) are ideal for this purpose.

For compounds **2**, **4**, and **5**, the triplet excited states were populated upon photoexcitation. These compounds were studied for the photooxidation of DHN (Figure 5). With photoirradiation by a xenon lamp, the absorption of DHN at 301 nm decreased and absorption of the oxidation product at 427 nm increased. Compound **5** shows the most substantial UV−vis absorption change upon photoirradiation (Figure 5b). In comparison, the photooxidation of DHN with $[Ir(ppy)_2(bpy)]PF_6$ (**Ir-1**, Scheme 1), which was used as the singlet oxygen sensitizer for photooxidation of DHN,[5] was also studied, but less significant UV−vis absorption change was observed. To quantitatively compare the photooxidation capability of the sensitizers, the photooxidation rates were studied by plotting the variation of the DHN concentration versus the irradiation time (Figure 5d). It was found that sensitizer **5** is the most efficient singlet O_2 sensitizer among the compounds studied here and shows a similar performance to the conventional triplet photosensitizer tetraphenylporphyrin (TPP).

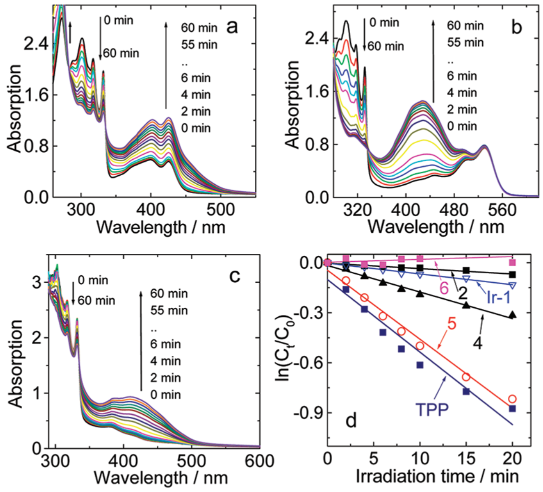


Figure 5. UV−vis absorption spectral change for the photooxidation of DHN using the NDI derivatives as the singlet oxygen ($^1O_2$) photosensitizer: (a) **4**, (b) **5**, (c) **Ir-1**. (d) Plots of $\ln(C_t/C_0)$ vs irradiation time (t) for the photooxidation of DHN with different sensitizers. c [sensitizers] = 3.6×10^{-5} M; [DHN] = 3.6×10^{-4} M; in dichloromethane/methanol (9/1, v/v), 20 °C.

Sensitizers **4** and **2** show a much weaker sensitizing capability due to the weak absorption of visible light by these compounds. It is interesting that Ir(III) complex **Ir-1** shows a much weaker photooxidation capability than **5** and TPP. The photostability of the sensitizers was also studied, and no significant bleaching was observed (see the Supporting Information).

The parameters of the photooxidation were compiled in Table 4. The photooxidation rate constant of **5** is similar to that of TPP. The Ir(III) complex, which was used as a sensitizer, shows a much smaller rate constant (k_{obs} = 6.6×10^{-3} min^{-1}). Thus, our result demonstrated that the tailored design of the organic triplet sensitizers can have a better effect than the transition-metal complex sensitizers. Furthermore, the light-harvesting ability of the sensitizers is also crucial for the photosensitizing. These results are useful for the design of new organic triplet photosensitizers.

Table 4. Photophysical Properties of the Triplet Sensitizers and the Rate Constants of Photooxidation of 1,5-Dihydroxylnaphthalene (DHN)[e]

sensitizers	λ_{abs}[a]	ε[b]	$\tau_T/\mu s$[c]	$k_{obs}/(10^{-2}\ min^{-1})$[d]
2	368, 410	2.2, 1.9	6.1	0.35
4	406, 428	0.9, 0.9	11.1	1.70
5	526, 496	2.1, 1.5	51.7	4.35
6	629	2.6		
Ir-1	285, 376	3.2, 0.6	0.8	0.66
TPP	416	29.7	82.5	4.32

[a] Absorption maxima; in nm (λ_{abs}). In toluene. [b] Molar extinction coefficient(ε). In 10^4 M^{-1} cm^{-1}; in toluene. [c] Triplet excited state lifetimes (τ_T), determined by transient absorption spectroscopy. In deaerated toluene. [d] Pseudo-first-order rate constant (k_{obs}); 20 °C. [e] In toluene (1.0×10^{-5} M).

2.6. Application of the Organic Triplet Sensitizers for Triplet−Triplet Annihilation Upconversion. The organic triplet sensitizers (Scheme 1) can also be used for other TTET processes, such as the TTA upconversion.[6−8,20,25−28] This kind of upconversion demonstrated advantages over the conventional upconversion methods, such as with two-photon absorption dyes (TPA) or rare earth materials, etc.[29,30] Triplet sensitizers and acceptors (annihilators) are combined in TTA upconversion.[6−8] The excitation energy is harvested by the triplet sensitizer, for which the triplet excited state is populated upon photoexcitation, via the cascade $S_0 \rightarrow S_n \rightarrow T_n \rightarrow T_1$ processes. The energy is then transferred to the triplet acceptor via the TTET process.[7] Examination of the mechanism of TTA upconversion indicates that triplet sensitizers with intense absorption of visible light and a long-lived triplet excited state are desired to improve the TTA upconversion efficiency.[7]

One of the major challenges for the current development of TTA upconversion is the limited availability of the triplet photosensitizers.[6a,7a,8a] Currently, the triplet sensitizers are limited to the transition-metal complexes, such as the Pt(II)/Pd(II) porphyrin complexes, the Pt(II)/Ir(III) complexes, etc.[6,7,20] However, similar to the development of the sensitizers for dye-sensitized solar cells (DSCs), to replace the transition-metal complex triplet photosensitizers with *organic* triplet photosensitizers will be the next milestone. However, the organic triplet photosensitizers for the TTA upconversion are rare and only a few sporadic examples have been reported.[9,27a,31] Recently we reported a BODIPY-based organic triplet photosensitizer library for TTA upconverion.[9] However, much room is left for development of organic triplet sensitizers; for example, the upconversion quantum yield observed with the known iodo-BODIPY triplet sensitizers is low (Φ_{UC} = 6.1%).[9] Thus, new organic triplet photosensitizers with higher upconversion quantum yields are desired.

Compounds **2**, **4**, and **5** show long-lived triplet excited states at RT, so these compounds were used as triplet sensitizers for TTA upconversion (Figure 6). Compound **5** shows strong absorption at the excitation wavelength (532 nm laser, CW). However, the emission of **5** is weak (Figure 6a). Compound **4** cannot be excited by the 532 nm laser. On the contrary, compound **6** shows intense fluorescence upon excitation with a 532 nm laser.

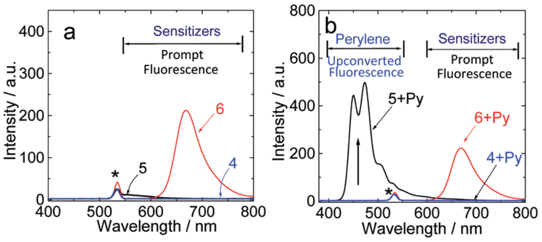


Figure 6. Upconversions with sensitizers **4**, **5**, and **6**. (a) Fluorescence emission of the sensitizers and perylene alone. (b) Emission of the sensitizers in the presence of triplet acceptor/annihilator perylene. Excited with a 532 nm laser (5.6 mW; power density is 70 mW cm^{-2}). The asterisks in (a) and (b) indicate laser scattering. In deaerated toluene; [Sensitizers] = 1.0 × 10^{-5} M; [Perylene] = 8.3 × 10^{-5} M; 20 °C.

Perylene was selected as the triplet acceptor.[7] In the presence of perylene, an intense blue emission in the range of 413−550 nm was observed with compound **5** as the triplet sensitizer (Figure 6b). Irradiation of perylene alone with a 532 nm laser does not produce the emission band in the range of 400−500 nm. This emission band is identical to the steady-state fluorescence emission spectrum of perylene (see the Supporting Information, Figure S33). Thus, the upconversion with compound **5** as the triplet sensitizer was verified.[7]

With compound **4** as the triplet sensitizer, no upconverted fluorescence was observed, due to the unmatched absorption of **4** and the 532 nm laser. This result demonstrated that the light-harvesting capability of the sensitizers is crucial for the TTA upcovnersion.[31] Interestingly, no upconversion was observed with compound **6** as the triplet sensitizer, despite the intense fluorescence of **6** upon excitation with a 532 nm laser. This lack of upconversion is within expectation because the triplet excited state of this compound cannot be populated upon photoexcitation. It is known that only the triplet excited state can initiate the TTET and thus the TTA upconversion.[6a,7a,8a]

The upconversion quantum yield (Φ_{UC}) with compound **5** as the triplet sensitizer was determined as 18.5%. To the best of our knowledge, this is the highest TTA upconversion quantum yield ever observed with organic triplet sensitizers. Previously, butadione was used as the organic triplet sensitizer.[31] However, the butadione has to be excited at a much shorter wavelength (442 nm), and the upconversion quantum yield was not reported. 2,4,5,7-Tetraiodo-6-hydroxy-3-fluorone was also used as the organic triplet sensitizer for TTA upconversion.[27] However, a very low upconversion quantum yield was reported (0.6%).[27a] The upconversion quantum yields with the NDI derivatives are also much higher than that with the iodo-BODIPY based organic triplet sensitizers (upconversion quantum yield is 6.1%).[9]

To confirm the delayed emission feature of the upconverted fluorescence of perylene in the TTA upconversion with compound **5** as the triplet photosensitizer, the decay of the upconverted emission at 470 nm was monitored (Figure 7). The lifetime of the upconverted emission of perylene was determined as τ = 146.6 μs, which is 5 orders of magnitude longer than the lifetime of the prompt fluorescence of perylene (τ = 4.1 ns, inset of Figure 6). Thus, the emission band observed in the TTA upconversion (Figure 6b) was the delayed fluorescence of perylene, that is, the upconverted emission.[27b]

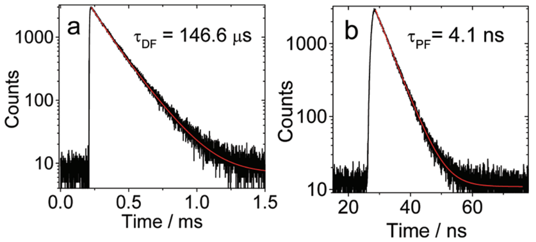


Figure 7. (a) Delayed fluorescence observed in the TTA upconversion with compound **5** as the triplet photosensitizer and perylene as the triplet acceptor. Excited at 530 nm (nanosecond pulsed OPO laser synchronized with spectrofluorometer) and monitored at 470 nm. Under these circumstances, compound **5** is selectively excited and the emission is due to the upconverted emission of perylene. (b) The prompt fluorescence decay of perylene determined in a different experiment (excited with picosecond 405 nm laser; the decay of the emission was monitored at 470 nm). In deaerated toluene; *c* [Sensitizers] = 1.0 × 10^{-5} M; *c* [Perylene] = 8.3 × 10^{-5} M; 20 °C.

The efficient TTA upconversion with compound **5** was confirmed by the upconversion intensity−excitation power relationship (Figure 8). A linear relationship, instead of the typical quadratic relationship, was observed (Figure 8b). It was proposed that a linear relationship can be observed if the TTET and the TTA upconversion are efficient.[9,27b]

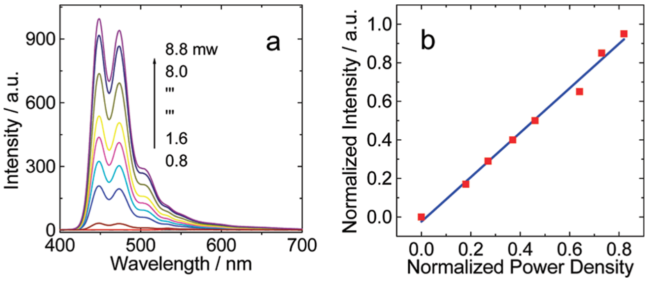


Figure 8. (a) Excitation power dependency of the upconverted perylene emission with compound **5** as the sensitizer (λ_{ex} = 532 nm. Continuous laser in toluene. (b) The normalized integrated emission intensity plotted as a function of normalized incident light power. The minimal and the maximal excitation power densities are 14.1 and 118.8 mW cm^{-2}, respectively. In deaerated toluene; *c* [Sensitizer] = 1.0 × 10^{-5} M; [Perylene] = 8.3 × 10^{-5} M; 20 °C.

The TTA upconversion with the organic triplet sensitizers is visible to unaided eyes (Figure 9). Compound **5** gives a very weak emission upon 532 nm laser excitation. In the presence of perylene, however, a bright blue emission of perylene was observed, which is due to the significant TTA upconversion with compound **5**. For compound **6**, however, the emission color does not change in the presence of perylene, due to the absence of TTA upconversion with compound **6**. With compound **4** as the triplet sensitizer, no upconversion can be observed. The CIE coordinates of the emissions of the photosensitizers and the upconversion were presented (Figure 9c,d).

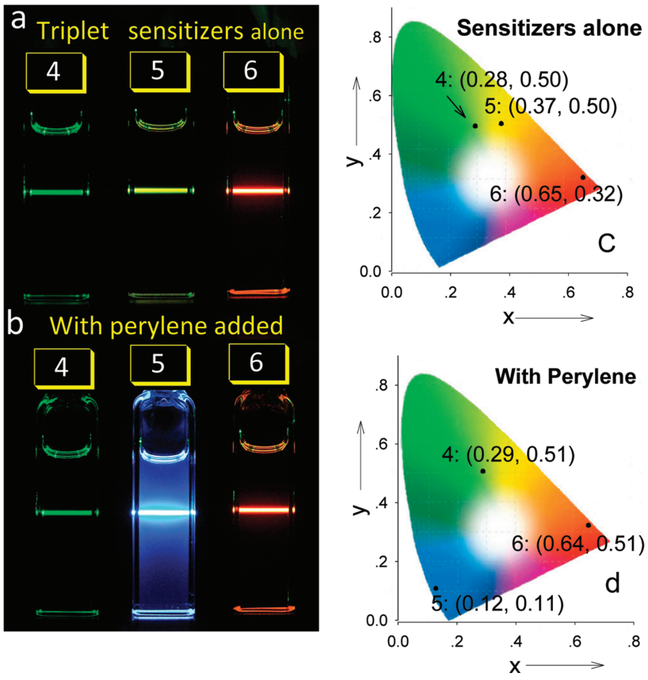


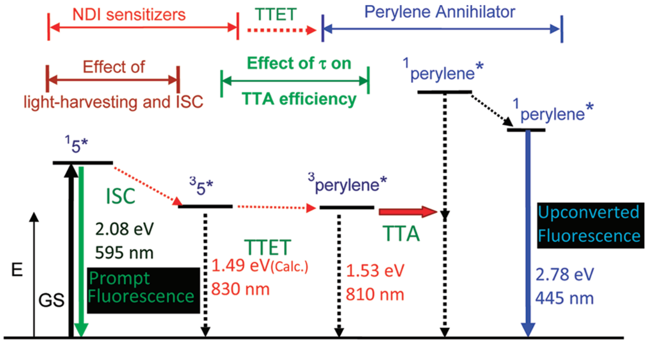
Figure 9. (a) Photographs of the emission of sensitizers alone and (b) the upconversion. (c) CIE diagram of the emission of sensitizers alone and (d) in the presence of perylene (upconversion). λ_{ex} = 532 nm (laser power: 5.6 mW); 20 °C.

The mechanism of the significant upconversion with compound **5** can be illustrated in Scheme 3. The singlet excited state of the sensitizers will be populated upon photoexcitation. The triplet excited state of the sensitizers will then be populated via the ISC process. The excitation energy was transferred to the triplet acceptor via the TTET process. The acceptors at the triplet excited states will then annihilate, and the singlet excited state of the acceptor is populated, from which the upconverted fluorescence emanates.[6]

It is obvious that two photophysical properties of the sensitizers are crucial for the TTA upconversion, that is, the light-harvesting capability and the lifetime of the triplet excited state. A strong light-harvesting effect of the sensitizer will produce more concentrated sensitizer molecules at the triplet excited state. Conversely, the long-lived T_1 excited state of the sensitizer will enhance the TTET process.[7,32]

2.7. Conclusions. Naphthalenediimide (NDI) derivatives with 2,6- or 2,3,6,7-tetrabromo or amino substituents were prepared, and the photophysical properties were studied with steady-state and time-resolved spectroscopy. 2,6-Dibromo NDI (compound **2**) and 2,3,6,7-tetrabromo NDI (compound **4**) show room-temperature phosphorescence at 610 nm (τ = 6.1 μs; Φ_P = 0.12%) and 667 nm (τ = 11.1 μs; Φ_P = 0.13%), respectively. 2,6-Dibromo-3,7-diamino NDI (compound **5**) shows strong absorption at 526 nm (ε = 21 000 M^{-1} cm^{-1}) and fluorescence at 551 nm (Φ_F = 0.2%); no RT phosphorescence was observed. Nanosecond time-resolved transient difference spectroscopy confirmed that the triplet excited state was populated upon photoexcitation. 2,3,6,7-Tetraamino NDI (**6**) shows fluorescence (λ_{em} = 668 nm; Φ_F = 16.2%), and no triplet excited state was populated upon excitation. Compounds **2**, **4**, and **5** were used as triplet photosensitizers for both the photooxidation of 1,5-dihydroxylnaphthalene (DHN) to produce juglone and triplet–triplet annihilation upconversions. We found that compound **5** is more efficient than the conventional photosensitizer $Ir(ppy)_2(Phen)[PF_6]$ for photooxidation of DHN. An upconversion quantum yield (Φ_{UC}) of 18.5% was observed with compound **5** as the organic triplet photosensitizer, which is much higher than the previously reported upconversion quantum yield with iodo-BODIPY based organic triplet photosensitizers (Φ_{UC} = 6.1%). Our results are useful for the design of organic triplet sensitizers for photocatalysis and upconversions, etc.

Scheme 3. Jablonski Diagram of Triplet–Triplet Annihilation (TTA) Upconversion with Bromo NDIs as Triplet Sensitizers (the Triplet States of Sensitizers and Acceptors Are Non-Emissive)[a]



[a] TTET stands for triplet–triplet energy transfer. Exemplified by **5**. ^{1}(compound **5**)* is the singlet excited state of compound **5**. ISC is intersystem crossing. ^{3}(compound **5**)* is the triplet excited state of compound **5**. TTET is triplet–triplet energy transfer. ^{3}perylene* is the triplet excited state of perylene. TTA is triplet–triplet annihilation. ^{1}perylene* is the singlet excited state of perylene. The emission bands observed in the TTA experiment are the simultaneous ^{1}(compound **5**)* emission (fluorescence) and ^{1}perylene* emission (fluorescence).

3. EXPERIMENTAL SECTION

3.1. Analytical Measurements. Luminescence quantum yields of the compounds were measured with quinine sulfate (Φ_F = 0.547 in 0.05 M sulfuric acid) and 4,4-difluoro-1,3,5,7-tetramethyl-8-phenyl-4-bora-3a,4a-diaza-*s*-indacene (Φ_F = 0.720 in THF) as the standard. Phosphorescence quantum yields of the compounds were measured with $Ru(Phen)(bpy)_2[PF_6]_2$ as the phosphorescence quantum yield standard (Φ_P = 0.060 in acetonitrile).[33]

3.2. Compounds B and C. Compounds **B** and **C** were synthesized according to literature methods.[13,35]

3.3. Synthesis of 1.[34] Naphthalene dianhydride (0.5 g, 1.87 mmol) was dissolved in freshly distilled DMF (5 mL). The slurry was heated to 135 °C under a N_2 atmosphere. 2-Ethylhexylamine (0.48 g, 3.73 mmol) was added to the above solution, and the reaction mixture was refluxed overnight, under a N_2 atmosphere. DMF was evaporated under reduced pressure, and the residue was dissolved in dichloromethane to remove the insoluble impurities. The solvent was evaporated under reduced pressure, and the crude material was purified by column chromatography (silica gel, dichloromethane). A white solid was obtained (512.8 mg; yield: 56%). mp 208.1–210.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (s, 4H), 4.10 (d, 4H, J = 16.0 Hz), 1.84–1.89 (m, 2H), 1.29–1.33 (m, 16H), 0.79–0.89 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.4, 131.2, 126.7, 98.5, 44.8, 38.1, 30.9, 28.8, 24.2, 23.2, 14.2, 10.8. ESI-HRMS ($[C_{30}H_{38}N_2O_4]^+$): calcd m/z = 490.2832. Found: m/z = 490.2861.

3.4. Synthesis of 2.[35] Under a N_2 atmosphere, a mixture of compound **B** (1.06 g, 2.5 mmol), 2-ethylhexylamine (0.97 g, 7.5 mmol), and acetic acid (25 mL) was stirred at 120 °C for 2 h. The mixture was cooled to rt and poured into cold water (100 mL). The precipitate was collected with filtration and washed with water. After drying under vacuum, the reddish solid was purified by column chromatography (silica gel; CH_2Cl_2/petroleum ether, 1:1, v/v). A yellow crystalline solid was obtained (530.1 mg; yield: 33%). mp 245.2–248.6 °C. ^{1}H NMR (400 MHz, $CDCl_3/CD_3OD$): δ 8.99 (s, 2H), 4.11–4.20 (m, 4H), 1.93–1.96 (m, 2H), 1.25–1.43 (m, 16H), 0.94 (t, 6H, J = 7.2 Hz), 0.89 (t, 6H, J = 7.2 Hz). ESI-HRMS ($[C_{30}H_{36}N_2O_4Br_2]^+$): calcd m/z = 646.1042. Found: m/z = 646.1032.

3.5. Synthesis of Compound 3.[11a] Under argon, diimide **2** (162.0 mg, 0.25 mmol) was heated in 2-ethylhexylamine (0.75 mL) at 140 °C for 2 h. The reaction mixture was cooled to rt, then poured into concentrated HCl (0.5 mL). The blue precipitate was collected and purified by column chromatography (silica gel; dichloromethane/hexane, 1:1, v/v). A blue crystalline solid was obtained (85.2 mg; yield: 45%). mp 144.2–146.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.44 (s, 2H), 8.17 (s, 2H), 4.08–4.18 (m, 4H), 3.43 (t, 4H, J = 12.0 Hz), 1.91–1.97 (m, 2H), 1.74–1.80 (m, 2H), 1.26–1.54 (m, 32H), 0.86–0.99 (m, 24H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.74, 163.73, 46.5, 44.1, 39.4, 38.0, 31.4, 30.9, 29.0, 28.8, 24.8, 24.2, 23.3, 23.2, 14.3, 14.2, 11.1, 10.9. ESI-HRMS ($[C_{46}H_{72}N_4O_4]^+$): calcd m/z = 744.5554. Found: m/z = 744.5524.

3.6. Synthesis of Compound 4.[12] A mixture of compound **C** (1.5 g, 2.6 mmol), *n*-octylamine (2.13 mL, 10.2 mmol), and acetic acid (30 mL) was stirred under a N_2 atmosphere for 40 min at 80 °C. The reaction mixture was cooled to rt and poured into water (200 mL); the solid was collected by filtration. The obtained yellow powder was washed with water (100 mL) and then petroleum ether (100 mL). After being dried under vacuum, a yellow solid state was obtained (2.1 g), which contains the intermediate product.[12] The crude product was used directly in the next reaction without further purification.

A solution of the intermediate (1.1 g) and PBr_3 (0.75 mL, 7.9 mmol) in dry toluene (50 mL) was refluxed for 10 h under a N_2 atmosphere. The mixture was cooled to rt and then poured into water (200 mL). The aqueous phase was extracted with toluene (3 × 100 mL), and the combined organic layers were dried over Na_2SO_4. The solvents were removed under reduced pressure, and the crude product was purified by column chromatography (silica gel; CH_2Cl_2/petroleum ether, 1/1, v/v). A yellow solid is obtained (297.2 mg; yield: 38%). mp 258–260 °C. ^{1}H NMR (400 M Hz, $CDCl_3$): δ 4.20 (t, J = 7.62 Hz, 4H), 1.72–1.79 (m, 4H), 1.37–1.42 (m, 8H), 1.28–1.35 (m, 12H), 0.88 (t, J = 6.96 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1, 135.7, 126.8, 125.8, 43.1, 32.0, 30.0, 29.4, 28.2, 27.3, 22.8, 14.3. ESI-HRMS ($[C_{30}H_{34}N_2O_4Br_4]^+$): calcd m/z = 801.9252. Found: m/z = 801.9311.

3.7. Synthesis of Compound 5.[36] A mixture of 2,3,6,7-tetrabromo-*N,N*′-dioctyl-naphthalene diimide **4** (100.0 mg, 0.12 mmol) and octylamine (32.0 mg, 0.24 mmol) in dry DMF (3 mL) was heated at 135 °C for 6 h. Completion of the reaction was monitored by TLC. After completion, DMF was removed on a rotary evaporator, and the product was purified by column chromatography on a flash silica column eluted with 1:1 DCM/hexane. **5** was obtained as orange red crystals (50.1 mg, 44%). mp 92–95 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.49 (s, 2H), 4.19 (t, 4H, J = 14.8 Hz), 3.58 (t, 4H, J = 14.8 Hz), 1.75–1.71 (m, 4H), 1.60–1.54 (m, 4H), 1.34–1.18 (m, 40H), 0.94–0.82 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4, 161.1, 151.1, 126.5, 124.9, 122.3, 102.8, 46.8, 41.6, 32.0, 29.2, 28.1, 27.0, 22.7, 14.2. ESI-HRMS ($[C_{46}H_{70}N_4O_4Br_2]^+$): calcd m/z = 901.3842. Found: m/z = 901.3870.

3.8. Synthesis of Compound 6.[36] The process is similar with the synthesis of **5**. Dark green crystals were obtained (40.2 mg, 33%). mp 93.1–96.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.46 (s, 4H), 4.21 (t, 4H, J = 16.0 Hz), 3.40 (t, 4H, J = 16.0 Hz), 1.71–1.74 (m, 4H), 1.48–1.55 (m, 8H), 1.21–1.31 (m, 60H), 0.82–0.88 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 147.1, 117.2, 108.1, 45.3, 40.5, 32.0, 29.4, 28.2, 27.3, 22.8, 14.3. ESI-HRMS ($[C_{62}H_{106}N_6O_4]^+$): calcd m/z = 998.8276. Found: m/z = 998.8185.

3.9. Nanosecond Time-Resolved Transient Difference Absorption Spectra. The nanosecond time-resolved transient absorption spectra were measured on an LP 920 laser flash photolysis spectrometer (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 argon gas flow was kept during the measurement.

3.10. Triplet–Triplet Annihilation Upconversions. A diode pumped solid-state (DPSS) continuous laser (532 nm) was used for the upconversions. The diameter of the 532 nm laser spot is ca. 3 mm. The power of the laser beam was measured with a VLP-2000 pyroelectric laser power meter. For the upconversion experiments, the mixed solution of the compound (triplet sensitizer) and perylene was degassed for at least 15 min with N_2 or Ar (note that the upconversion can be significantly quenched by O_2). The solution was then excited with a laser. The upconverted fluorescence of perylene was observed with the spectrofluorometer. To repress the scattered laser, a black box was put behind the fluorescent cell to trap the laser beam.

The upconversion quantum yields (Φ_{UC}) of compound **5** were determined with the prompt fluorescence of compound **6**. The upconversion quantum yields were calculated with the following equation, where Φ_{UC}, A_{sam}, I_{sam}, and η_{sam} represent the quantum yield, absorbance, integrated photoluminescence intensity, and the refractive index of the samples and the solvents (eq 1, where the subscript "std" is for the standard used in the measurement of the quantum yield and "sam" for the samples to be measured). The equation is multiplied by a factor of 2 in order to make the maximum quantum yield to be unity.[6a] All these data were independently measured three times (with different solution samples).

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

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 the software of CIE Color Matching Linear Algebra.

The delayed fluorescence feature of the upconversion was measured with a nanosecond pulsed laser (Opolett 355 II+UV nanosecond pulsed laser; typical pulse length, 7 ns; pulse repetition, 20 Hz; peak OPO energy, 4 mJ. Wavelength is tunable from UV to 2200 nm; OPOTEK, USA), which is synchronized to an FLS 920 spectrofluorometer (Edinburgh, U.K.). The pulsed laser is sufficient to sensitize the TTA upconversion. The decay kinetics of the upconverted fluorescence (delayed fluorescence) was monitored with an FLS920 spectrofluorometer (synchronized to the OPO nanosecond pulse laser). The prompt fluorescence lifetime of the triplet acceptor perylene was measured with an EPL picosecond pulsed laser (405 nm), which is synchronized to the FLS 920 spectrofluorometer.

3.11. DFT Calculations. The density functional theory (DFT) calculations were used for optimization of the geometries at both singlet states and triplet states. The energy level of the T_1 state (energy gap between S_0 state and T_1 state) was calculated with the time-dependent DFT (TDDFT), based on the optimized singlet ground-state geometries (S_0 state). All the calculations were performed with Gaussian 09W.[37]

■ ASSOCIATED CONTENT

Supporting Information

The synthesis and structural characterization data of the fluorophores and DFT calculation information. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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