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Bodipy Derivatives as Organic Triplet Photosensitizers for Aerobic Photoorganocatalytic Oxidative Coupling of Amines and Photooxidation of Dihydroxylnaphthalenes

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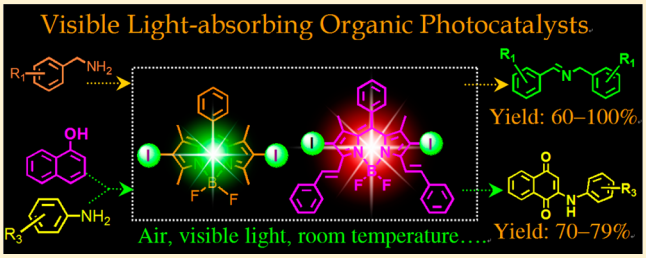
Supporting Information

ABSTRACT: We used iodo-Bodipy derivatives that show strong absorption of visible light and long-lived triplet excited states as organic catalysts for photoredox catalytic organic reactions. Conventionally most of the photocatalysts are based on the off-the-shelf compounds, usually showing weak absorption in the visible region and short triplet excited state lifetimes. Herein, the organic catalysts are used for two photocatalyzed reactions mediated by singlet oxygen ($^1O_2$), that is, the aerobic oxidative coupling of amines and the photooxidation of dihydroxylnaphthalenes, which is coupled to the subsequent addition of amines to the naphthoquinones, via C−H functionalization of 1,4-naphthoquinone, to produce *N*-aryl-2-amino-1,4-naphthoquinones (one-pot reaction), which are anticancer and antibiotic reagents. The photoreactions were substantially accelerated with these new iodo-Bodipy organic photocatalysts compared to that catalyzed with the conventional Ru(II)/Ir(III) complexes, which show weak absorption in the visible region and short-lived triplet excited states. Our results will inspire the design and application of new organic triplet photosensitizers that show strong absorption of visible light and long-lived triplet excited state and the application of these catalysts in photoredox catalytic organic reactions.



1. INTRODUCTION

Triplet photosensitizers-promoted photoredox catalytic organic reactions have attracted much attention,[1−6] such as the aza-Henry reaction,[7] the oxidative coupling of amine or the cross-dehydrogenative coupling reactions,[8−10] and hydrogen (H_2) production by photolysis of water.[11−13] The photosensitizers used for these reactions are usually the off-the-shelf compounds, such as the $Ru(bpy)_3[PF_6]_2$ (bpy = 2,2′-bipyridine) or $Ir(ppy)_3$ complex (ppy = 2-phenylpyridine),[14] or organic triplet photosensitizers, such as Eosin Y or benzophenone.[9] Inorganic metarials, such as polycrystalline cadmium sulfide, was also used for the photoredox catalytic organic reactions.[1e,g] Recently, Eosin Y was used for intermolecular α-alkylation of aldehydes and direct C−H arylation of heteroarenes with aryl diazonium salts[15] and dehydrogenative coupling reactions of amines with nitroalkanes.[16] Rose Bengal (RB) was also used for dehydrogenative coupling reactions of amines with nitroalkanes.[17] However, the π-conjugation framework of these known organic photocatalysts is difficult to be modified; thus, the absorption wavelength of these catalysts cannot be readily shifted to the red end of the spectrum.

The common feature of these off-the-shelf photosensitizers is weak or moderate absorption of visible light, and the difficulty to modify the molecular structures of the photocatalysts to optimize the catalytic property. For example, the molar absorption coefficient ε of Ru(II) complexes is usually less than 20000 M^{-1} cm^{-1} at ca. 450 nm,[1−13] and the absorption wavelength of the typical Ru(II) and Ir(III) complexes is below 450 nm. Triplet photosensitizers with absorption in a longer wavelength region for photocatalysis were rarely reported. Furthermore, the redox properties of these photosensitizers are not readily tunable. Therefore, it is highly desired to develop new organic photosensitizers that show easily derivatizable molecular structures to promote the photoreactions. To date, very few organic triplet photosensitizers have been used for photocatalytic reactions, such as oxidative coupling of amines.[8b] To the best of our knowledge, no photocatalytic organic reaction was carried out with organic photocatalyts that show strong absorption in the visible region and readily changeable molecular structures.[2,8,18]

The organic photosensitizers for photocatalysis should have the following properties: (1) strong absorption of visible light, preferably in green and red regions of the spectrum; (2) the triplet excited state should be efficiently populated upon photoexcitation; (3) the lifetime of the triplet excited state should be long so that the single electron transfer (SET, the most popular mechanism for photocatalytic organic reactions) will be improved; (4) the molecular structure of the triplet photosensitizers (photocatalysts) should be readily tunable, so that the photophysical and electrochemical properties can be optimized.

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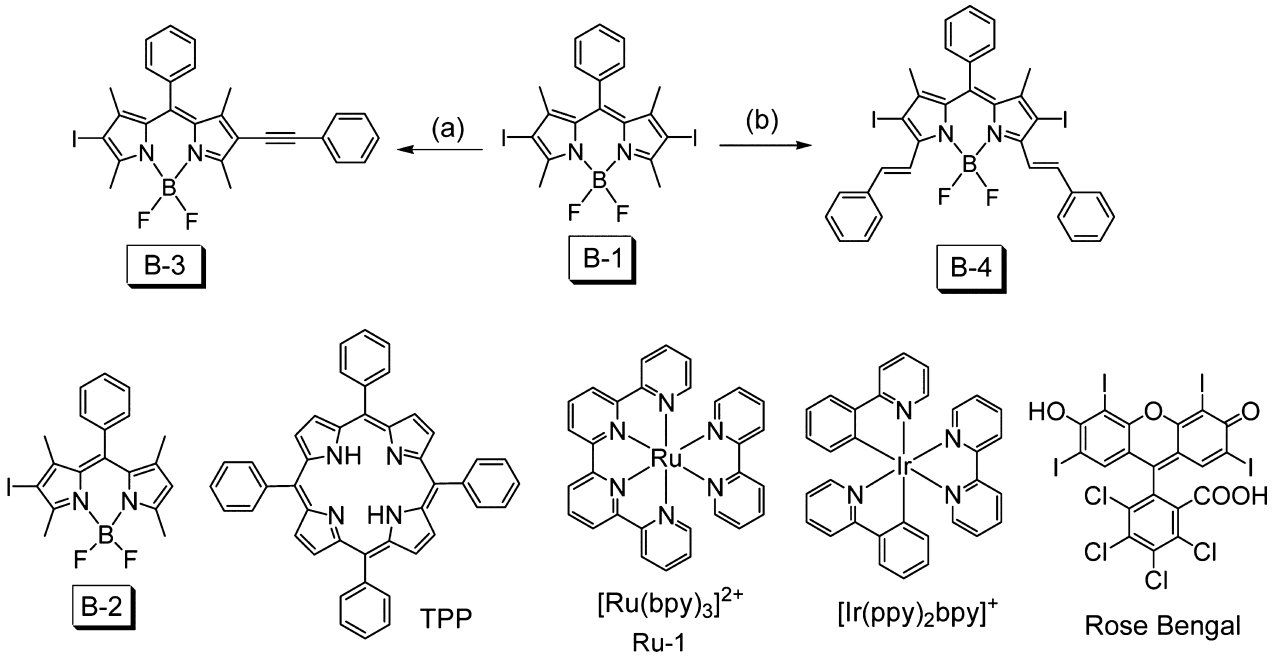
Scheme 1. Synthesis of B-3 and B-4[a]



[a]Known compounds **B-1**, **B-2**, TPP, **Ru-1**, **Ir-1** and Rose Bengal are presented. Key: (a) $Pd(PPh_3)_2Cl_2$, CuI. Yield 35%. (b) Piperidine, AcOH, DMF, microwave. Yield: 42%.

In order to address the above challenges, herein we prepared a series of iodo-Bodipy as triplet photosensitizers that show the aforementioned desired photophysical properties (**B-1**−**B-4**, Scheme 1). We proved that these organic triplet photosensitizers can be used to promote different types of photocatalytic reactions, such as the aerobic oxidative coupling of amines and photooxidation of dihydronaphthalenes.[19] These photocatalytic reactions give a synthetically important products, such as Schiff base by C−N bond formation,[8] and naphthoquinones,[19] and thereafter the C−H functionalization of 1,4-naphthoquinone to produce *N*-aryl-2-amino-1,4-naphthoquinones (one-pot reaction), which are anticancer and antibiotic reagents.[20] Previously the above photoreactions were often carried out with the conventional Ru(II) or Ir(III) complexes as photocatalysts. With the new iodo-Bodipy based triplet photosensitizers, for which the molecular structure is readily changeable, which is different from the known organic photocatalysts such as Eosin Y, these different reactions are greatly accelerated, indicated the significance of using organic triplet photosensitizer. Our approach will be very useful for the development of photocatalytic reactions.

2. RESULTS AND DISCUSSION

2.1. Design and Synthesis of the Photocatalysts. The design rationales of the photocatalysts are (1) strong absorption of visible light; (2) high triplet state quantum yield; (3) long-lived triplet excited states; and (4) readily changeable molecular structures. Strong absorption of visible light and efficient production of long-lived triplet excited states will ensure abundent photocatalysts at the excited state, which are beneficial for the energy transfer or the electron transfer between the photocatalyst and the substrate molecules.[1,2] To fufill these goals, Bodipy was selected as the chromophore for preparation of the organic photocatalysts (Scheme 1), owing to its ideal photophysical properties, such as strong absorption of visible light, good photostability, and versatile derivatizing chemistry.[21−24] In order to ensure efficient intersystem crossing (ISC), by which the triplet excited state was produced, iodine atoms were attached on the π-core of Bodipy chromophore, instead of the peripheral of the chromophore (such as the meso phenyl moiety).[25−27] The absorption wavelength of the Bodipy-based triplet photosensitizer can be readily red-shifted by attaching a styryl moiety to the Bodipy chromophore (**B-4**). The compounds were obtained in satisfactory yields.

2.2. Steady State UV−Vis Absorption and Fluorescence Spectra. The UV−vis absorption of the organic photocatalysts and the reference compounds were studied (Figure 1). For the conventional photosensitizer Ru-

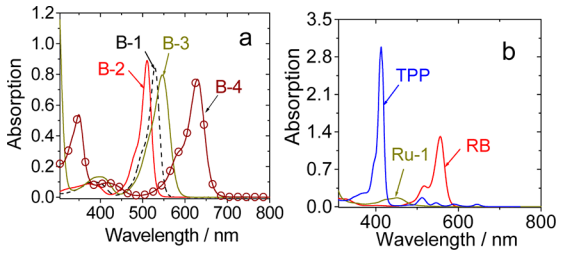


Figure 1. (a) UV−vis absorption spectra of (a) **B-1**−**B-4** and (b) TPP, **Ru-1** and RB. In CH_3CN, (1.0×10^{-5} M; 22 °C).

$(bpy)_3[PF_6]_2$, moderate absorption in the visible range were observed (ε = 16700 M^{-1} cm^{-1} at 451 nm). For the Bodipy-based organic photocatalysts **B-1**−**B-4**, however, much more intense absorption in the red-shifted range was observed; the molar absorption coefficients are up to 89000 M^{-1} cm^{-1} in the range of 511−630 nm. The lifetimes of the triplet excited states were determined as 1.8−84.6 μs (Table 1). The photophysical properties of the triplet photosensitizers (the photocatalysts) are compiled in Table 1.

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Table 1. Photophysical Parameters of the Photocatalysts (Triplet Photosensitizers)[a]

	λ_{abs}/nm	ε^b	λ_{em}/nm	Φ_F/%[c]	$\tau/\mu s^d$	Φ_Δ/%[e]
B-1	529	0.85	548	2.7	84.6	0.79
B-2	511	0.89	535	3.6	80.4	0.79
B-3	547	0.80	585	14.6	85.2	0.86
B-4	630	0.77	654	5.1	1.8	0.69
RB	556	1.31	575	29.0	117.6	0.80
TPP	411	3.08	655	10.0	70.0	0.62
Ru-1	451	0.167	607	6.1	0.45	0.57

[a]In CH_3CN (1.0×10^{-5} M). [b]Molar extinction coefficient at the absorption maxima. ε: 10^5 M^{-1} cm^{-1}. [c]With Bodipy as the standard (Φ = 0.72 in THF). [d]Triplet state lifetimes, measured by transient absorption spectra, in μs. [e]Singlet oxygen quantum yield. With Rose Bengal (RB) as the standard (Φ_Δ = 0.8 In Methanol), 22 °C.

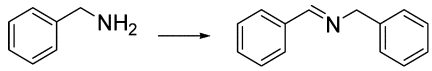
Notebly **B-4** shows a short triplet excited state lifetime (1.8 μs), but the singlet oxygen quantum yield (Φ_Δ = 0.69) is comparable to that of **B-1** (Table 1). The most probable reason is that the lifetime of **B-4** (1.8 μs) is already long enough to efficiently produce singlet oxygen ($^1O_2$) in fluid solution at room temperature, by the triplet−triplet-energy-transfer process. Therefore, there is no drastic difference for the singlet oxygen quantum yield of the triplet photosensitizers that are with different triplet state lifetimes. Similar results were observed previously. For example, $Ir(ppy)_2(bpy)$ complex is with short-lived triplet excited state (0.34 μs), but the $^1O_2$ quantum yield is high (Φ_Δ = 0.97).[19] However, singlet oxygen photosensitizing is dependent not only on the singlet oxygen quantum yield but also on the visible light-absorbing property of the photosensitizers.

We investigated the UV−vis absorption spectrum of **B-4** upon monochromatic light irradiation but found no changes for the UV−vis absorption spectra. Therefore, we propose that there is no significant cis−trans isomerization for the styryl C=C bonds in **B-4** (Supporting Information, Figure S91).

2.3. Photocatalytic Oxidative Coupling of Amines. First the iodo-Bodipy triplet photosensitizers were used for oxidative coupling of amines. Recently, inorganic material of carbon nitride and prophyrin derivatives used as the photosensitizer for the photocatalytic oxidative coupling of amines was reported.[1f,8] With carbon nitride as the photocatalysts, the reaction was performed at 80 °C and 0.5 MPa O_2. However, the ideal reaction condition will be at room temperature and using air as the oxidant.[14] Furthermore, the absorption of the mesoporous graphite carbon nitride in visible range is not strong, especially in the range beyond 450 nm.[8] Recently phenothiazine derivatives were used as photocatalysts for oxidative coupling of amines, but the absorption of those dyes are in the blue region and the reaction was carried out under neat O_2 and a long reaction time was mandatory (20 h).[8b] With porphyrin compounds, good results were obtained, such as fast photocatalytic reaction.[1f] However, it is clear that much room is left to increase the molecular divercity of the photocatalysts.

Interestingly, with the organic triplet photosensitizers, we found that the oxidative coupling of benzyl amine can be carried out at much milder conditions compared to that with the mpg-C_3N_4.[8a] For example, the reaction can be run in aerated solution (not neat O_2 atmosphere) at one atmosphere pressure (1 atm), 22 °C and the reaction was completed within one hour. The conversion and selectivity are excellent (Table 2). In comparison, with mpg-C_3N_4 as the photosensitizer, the same reaction has to be run at 5 atm neat O_2 atmosphere (not air), elevated temperature (80 °C) and with prolonged reaction time (2−5 h).[8] Furthermore, we found that the typical off-the-shelf organic triplet photosensitizers, such as TPP, Rose Bengal (RB), $[Ir(ppy)_2(bpy)]PF_6$ and **Ru-1** (Scheme 1), give lower conversion (12−81%). On the contrary, the Bodipy-based triplet photosensitizers give quantitative conversion of the benzyl amine to the imine (Table 2).

Table 2. Transformation of Benzylamine Catalyzed by Different Triplet Photosensitizers[a]



entry	photosensitizer	solvent	T (°C)	t (h)	conv. (%)[b,c]
1	Rose Bengal	acetonitrile	20	1	81
2	**B-1**	acetonitrile	20	1	100
3	**B-2**	acetonitrile	20	1	100
4	**B-3**	acetonitrile	20	1	100
5	**B-4**	$MeCN/CH_2Cl_2$ (3:2, v/v)	25	1	100
7	**TPP**	acetonitrile	20	1	11
8	**TPP**	CH_2Cl_2	20	1	57
9	$Ru(bpy)_3$	acetonitrile	25	1	58
7	$Ir(ppy)_2bpy$	acetonitrile	20	1	37

[a]Reaction conditions: benzylamine (0.5 mmol), photosensitizers catalyst (0.005 mmol, 1 mol %), solvent (5 mL), in air, λ > 380 nm (20 mW/cm^2), 1 h, 22 °C. [b]Yield was determined with ^1H NMR. [c]Reaction was monitored by TLC. Only two spots were found (except photosensitizer), therefore the selectivity of the photoreaction is good.

The reaction show excellent tolerance of functional groups on the amines used as the substrates for the oxidative coupling reaction (Table 3). Moderate to excellent conversion and selectivity were observed. For example, with triplet photosensitizer **B-1** as the photocatalyst and 4-*tert*-butylbenzylamine as the substrate, 100% conversion was observed (entry 4 in Table 3). Furthermore, hydroxyl amine (entry 6, Table 3) was also used as the substrate. The hydroxyl group was not oxidized and demonstrated the good functional group-tolerance of the photooxidation with the Bodipy photosensitizers. Heterocyclic amine, such as pyridyl methylamine, also proceed smoothly (Table 2, entry 3). No reaction was found with amine lacking of α-H, such as aniline (entry 9 in Table 3). Regioselective oxidations were observed with unsymmetrical secondary amines (entries 5 and 8 in Table 3); the reaction proceeded to yield the conjugated *N*-benzylidene products in remarkably high selectivity rather than those generated from oxidation on the less activated site (entry 5, 6 and 8, Table 3). This observation is in agreement with previouse results.[1f] We propose that the intermediate at the aryl side (such as radical, due to the hydrogen absraction by $^1O_2$) is more stable than that at the alkyl chain side. As a result, only the aryl imine was produced for the asymmetrical amines. We also found that the benzylamines with electro-donating substituents give higher yields than the benzylamines with electron-withdrawing substituents (entries 2, 7−9, Table 3). The photooxidation with other triplet photosensitizers were carried out (see Supporting Information for detail). The reaction was also run on 1 g scale, yield up to 95% was obtained (Supporting Information).

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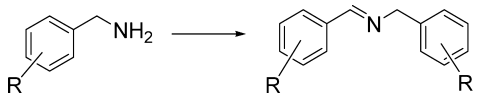
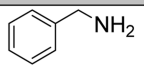
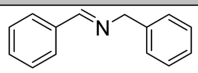
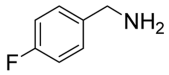
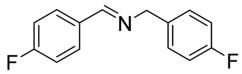
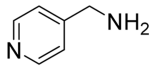
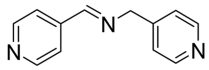
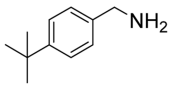
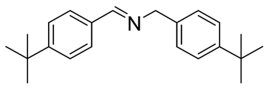
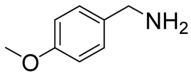
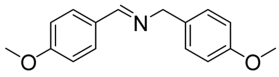
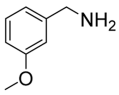
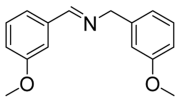
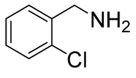
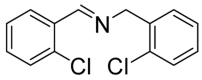
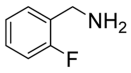
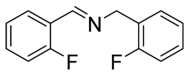
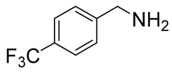
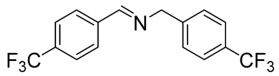
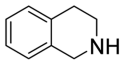
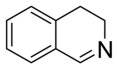
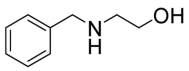
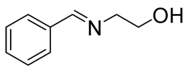
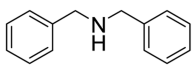
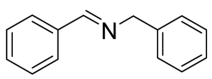
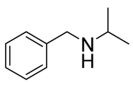
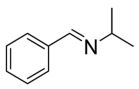
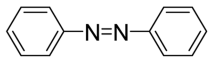
Table 3. Oxidation of Various Amines using B-1[a]



Entry	Substrate	Product	*t* [h]	Yield%[b]	TON[d]	TOF / min^{-1} [e]
1			1.0	100	100	1.6
2			0.5	60	60	1.0
3			1.0	91	91	1.5
4			1.0	100	100	1.6
5			1.0	89	89	1.5
6			1.0	100	100	1.7
7			1.0	100	100	1.7
8			2.0	44	44	0.4
9			2.0	66	66	0.6
10			2.5	74	74	1.2
11			2.5	62	62	0.4
12 [f]			4.0	100	100	0.4
13 [f]			4.0	100	100	0.4
14			3.0	– [c]	–	–

[a]Reaction conditions: benzylamine (0.5 mmol), photosensitizers catalyst (0.005 mmol, 1 mol %), solvent (5 mL), in air, $\lambda > 380$ nm (20 mW/cm^2), 1 h, 22 °C. [b]Yield was determined with ^{1}H NMR. [c]No reaction. [d]Turnover number, calculated by the ratio of moles of product/mol of catalyst. [e]Turnover frequency. [f]Photoirradiation power density is 37 mW/cm^2.

The experiments indicated that oxygen (O_2), photoirradiation, and the triplet photosensitizers are all essential for the photocatalytic oxidative coupling of the amines (entries 1−4, Table 4). The photocatalytic oxidation was greatly inhibited in the presence of histidine, a $^1O_2$ scavenger. In the presence of superoxide dismutase (SOD), however, the photooxidation proceeded as normal. Therefore, we propose that the presence of $^1O_2$ is responsible for the photooxidation. $O_2^{-\bullet}$ is not involved in the photocatalytic oxidative coupling of the amines, which is supported by the fact that the reaction cannot be suppressed by 2,6-di-*tert*-butylmethylphenol.[8a]

The reaction mechanism of the photocatalytic oxidative coupling reaction were studied by electron spin resonance (ESR) (Figure 2). 5,5-Dimethyl-1-pyrroline-noxide (DMPO) and 2,2,6,6-tetramethylpiperidine (TEMP) were employed as a probe to react with $O_2^{-\bullet}$ and $^1O_2$, respectively.[9]

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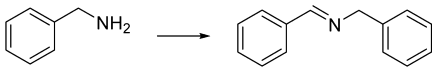
Table 4. Mechanism Study of Oxidation Amines using B-1[a]



entry	condition	solvent	*t* (h)	yield (%)[b]
1	In air	acetonitrile	1	99
2	In N_2	acetonitrile	3	–[c]
3	No photoirradiation	acetonitrile	3	–[c]
4	No **B-1**	acetonitrile	3	4
5	3 equiv TFA	CH_2Cl_2	3	–[c]
6	2,6-di-*tert*-butylmethylphenol (0.05 mmol)	acetonitrile	1	70
7	2 equiv Histidine	THF/H_2O = 1/2	1	9
8	No histidine	THF/H_2O = 1/2	1	80
9	SOD (2 equiv)[d]	acetonitrile	1	100

[a]General reaction is applicable to entries **1**–**6**. Reaction conditions: various amines (0.5 mmol), photosensitizers catalyst **B-1** (0.005 mmol, 1 mol %) were dissolved in different solvents. The mixture was irradiated with 35 W xenon lamp (λ > 380 nm 20 mW/cm^2). [b]Yields were determined by ^{1}H NMR spectrum. [c]No reaction. [d]SOD stands for superoxide dismutase.

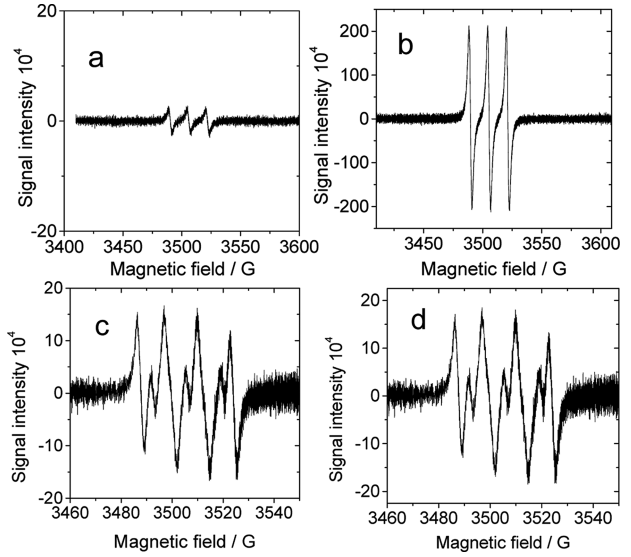


Figure 2. ESR spectrum of the mixtures upon photoirradiation. (a) **B-1** (1.0×10^{-4} M), benzylamine (1.5×10^{-3} M) and TEMP (0.12 M); (b) **B-1** (1.0×10^{-4} M) and TEMP (0.12 M); (c) **B-1** (1.0×10^{-4} M), DMPO (2.0×10^{-2} M), benzylamine (1.5×10^{-3} M); (d) **B-1** (1.0×10^{-4} M), DMPO (2.0×10^{-2} M). In air-saturated CH_3CN. The samples were photoirradiated with 532 nm laser for 20 s (141 mW/cm^2). At 22 °C.

For the mixture of **B-1** and TEMP, signal of the $^1O_2$-TEMP adduct was detected upon photoexcitation (Figure 2b). In the presence of benzylamine, however, the magnitude of the signal was greatly attenuated (Figure 2a), indicating that the $^1O_2$ was consumed in the presence of benzylamine; therefore, the oxidative coupling of the benzylamine was mediated by $^1O_2$. With DMPO, however, the signal of the DMPO-$O_2^{-\bullet}$ adduct did not change in the presence of benzylamine, indicating that $O_2^{-\bullet}$ was not involved in the photocatalytic reaction.

The reaction mechanism of the $^1O_2$-mediated aerobatic oxidative coupling of the amines is summarized in Scheme 2.[1f] $^1O_2$ was produced by the triplet photosensitizers. Then the amine was oxidized to the imine and hydrogen peroxide (H_2O_2) was produced. Reaction of the imine with another molecule of amines produced the Schiff base product. NH_3 was produced as a side product.[1f] We studied the photocatalytic reaction in $CDCl_3$/$CHCl_3$.[1f] Previously it was found that the photocatalytic reaction proceeded with higher velocity in deuterated solvents because the lifetime of $^1O_2$ is longer in deuterated solvent than in their proteated counterparts.[1f] We also observed much higher reaction velocity in $CDCl_3$ than that in $CHCl_3$ (see Supporting Infomration, Table S7). This result indicated that $^1O_2$ is involved in the photocatalytic reactions. Moreover, as a proof of the proposed mechanism, H_2O_2 was detected by using KI/CH_3COOH. A brown color was observed by mixing the photocatalytic reaction mixture and KI/CH_3COOH (see Supporting Information, Figure S90).[1f] Furthermore, the effect of DABCO (1,4-diazabicyclo[2.2.2]-octane, a singlet oxygen scanvenger) on the photocatalytic oxidative coupling of benzylamines was also studied. We found that the photocatalytic reaction can be significantly surpressed by the DABCO (Supporting Information, Table S8).[1f] Therefore, $^1O_2$ is involved in the photocatalytic reaction. All of these results support the proposed mechanism (Scheme 2).

2.4. Photocatalytic Oxidation of Dihydroxylnaphthalene. In this section, we will demonstrate that the application of organic triplet photosensitizers is not limited to the photocatalytic oxidative coupling of amines. Singlet oxygen ($^1O_2$) can be produced by the triplet photosensitizers in the presence of O_2.[28−35] Therefore, the $^1O_2$-mediated photocatalytic oxidation of 1,5-dihydroxylnaphthalene (DHN) was studied. The reaction can be followed by monitoring the UV−vis changes (Figure 3).[19] The product of the photooxidation of DHN, naphthoquinones, such as juglone, and thereafter the C−H functionalization of 1,4-naphthoquinone gave *N*-aryl-2-amino-1,4-naphthoquinones, which are anticancer and antibiotic reagents.[20] Previously cyclometalated Ir(III) complexes were used as triplet photosensitizers for photooxidation of DHNs, but the Ir(III) complexes show weak absorption in the visible region.[19]

Recently we reported some visible light-harvesting transition metal complexes as triplet photosensitizers for photooxidation of DHNs.[36−38] Iodo-aza Bodipy was used as triplet photosensitizers for photooxidation of DHNs, but the photooxidation was not studied in detail.[39] Herein we studied the photooxidation of DHNs with various organic triplet photosensitizers. The photooxidation was also coupled with the one-pot preparation of amine adducts of the naphthoquinones, which can be potentially used as anticancer reagents.[20]

First we investigated a few naphthols as the substrates, such as 1-naphthol, 1,5-DHN and 1,6-DHN. In all cases, the yields of the naphthoquinones are satisfactory (Table 5). In order to explore the application of the photooxidation of DHN for preparation of more functionalized products, the photooxidation of DHN was coupled to the adduction of aromatic amines into a one-pot reaction (Table 6).[40]

In the first step of the reaction, the naphthol was oxidized to naphthoquinones. Then without isolation, aromatic amines and Cu^{2+} salts were added and the adduction products amino-naphthoquinones were obtained.[20] The one-pot reaction was optimized with TPP as the triplet photosensitizer (Supporting Information, Table S6). The result shows that the optimal reaction conditions for the one-pot preparation of amino-naphthoquinones are 1.5 h for the first step and 3 h reaction time for the second step of the one-pot reaction. The reactions

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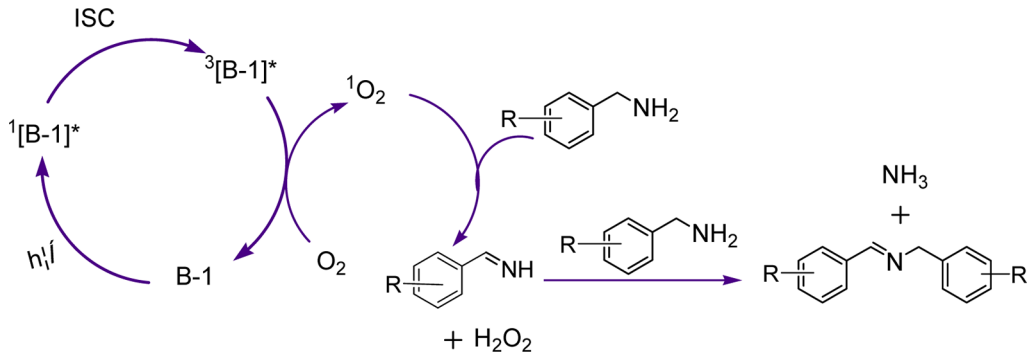
Scheme 2. Proposed Reaction Mechanism for the Photocatalytic Aerobatic Oxidation of Amines with the Triplet Photosensitizers B-1−B-4



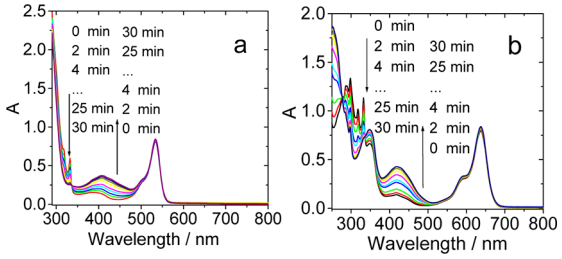
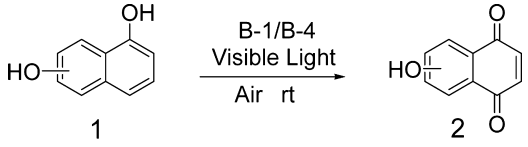


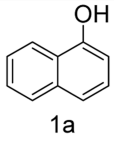
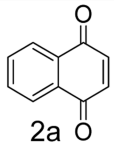
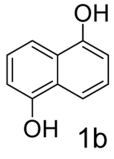
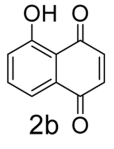
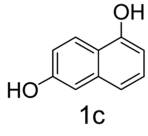
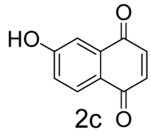
Figure 3. UV−vis absorption spectral changes for the photooxidation of DHN. (a) **B-1** as a sensitizer. (b) **B-4** as a sensitizer (in CH_2Cl_2/MeOH, 9:1, v/v). c[sensitizers] = 1.0×10^{-5} M. c[DHN] = 1.0×10^{-4} M. Light intensity: 20 mW/cm^2, 20 °C.

were carried out at 65 °C. The reaction is tolerant to aromatic amine substrates with various functional groups (see Supporting Information for the substrate tolerance study). However, 4-nitroaniline failed to produce the aminonaphthoquinone (Supporting Information, Figure S5). Furthermore, we found that $CuSO_4$ and CuCl can catalyze the reaction with high efficiency. Previously only $Cu(AcO)_2$ was used as the catalyst.[40]

With **B-1** as the triplet photosensitizer, we found that the yields of the aminonaphthoquinones are generally higher than that with TPP as the triplet photosensitizer (Table 6). The yields of the aminonaphthoquinones are generally higher than 70%. We attribute the more efficient photooxidation with **B-1** to the stronger visible light-harvesting ability of **B-1** in the visible region. These results are promising for preparation of

Table 5. Photooxidation of Naphthol with B-1 and B-4[a]



Entry	Substrate 1	Product 2	Yield [b]	TON [c]	TOF/ min^{-1} [d]
1	 1a	 2a	74/81	37/40	0.6/0.7
2	 1b	 2b	73/77	36/38	0.6/0.6
3	 1c	 2c	80/87	40/43	0.7/0.7

[a]Reaction conditions: substrate **1** (0.10 mmol), photocatalyst **B-1**/**B-4** (2 mol %), in CH_2Cl_2/CH_3OH(v/v, 4:1, 5.0 mL). The reaction mixture was irradiated with 35 W Xe lamp for 30 min (0.72 M $NaNO_2$ solution was used as filter so that light with wavelength λ < 385 nm was blocked. The light intensity at the photoreactor is 20 mW/cm^2). At 20 °C. [b]Yield of the isolated products with **B-1** and **B-4** as the triplet photosensitizers. [c]Turnover number, calculated by the molar ratio of the production and the catalysts. [d]Turnover frequency.

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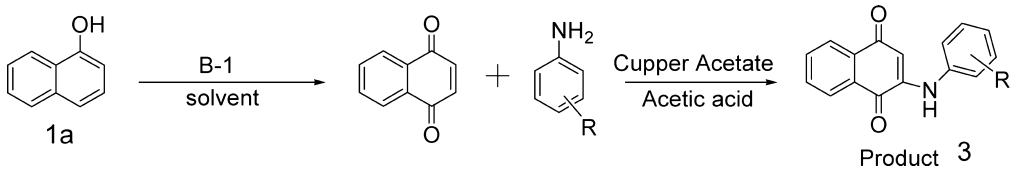
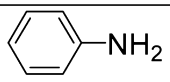
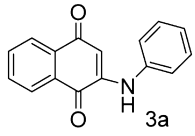
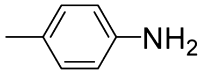
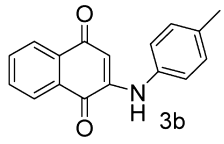
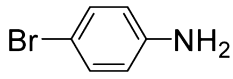
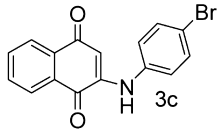
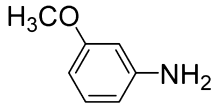
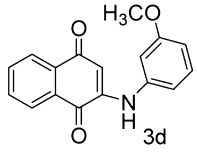
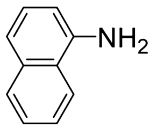
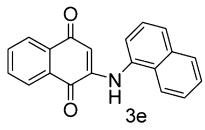
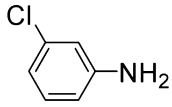
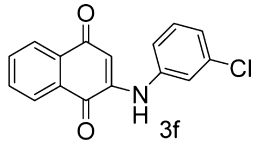
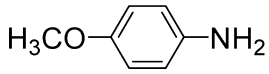
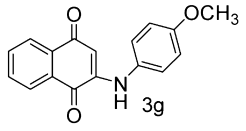
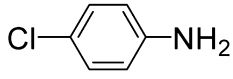
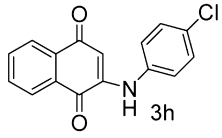
Table 6. Photooxidation of Naphthol with B-1 and Aniline Addition to the Naphthoquinones[a]



Entry	Aniline derivatives	Product	Yield%[b]
1			75
2			71
3			48
4			74
5			79
6			77
7			73
8			70

[a]Step 1: Naphthol (0.5 mmol) and photosensitizer **B-1** (5 mol %) were mixed in $CHCl_3$/Methanol (10 mL, 4/1, v/v). The mixture was irradiated with 35W Xe lamp (λ > 385 nm, 30 mW/cm^2) for 0.5 h. Step 2: aniline derivatives (0.6 mmol), acetic acid (10 mL) and $Cu(AcO)_2$ (10 mol %) were added into the solution and the mixture was heated at 65 °C for 3 h. [b]Overall yield of the isolated product, calculated based on naphthol.

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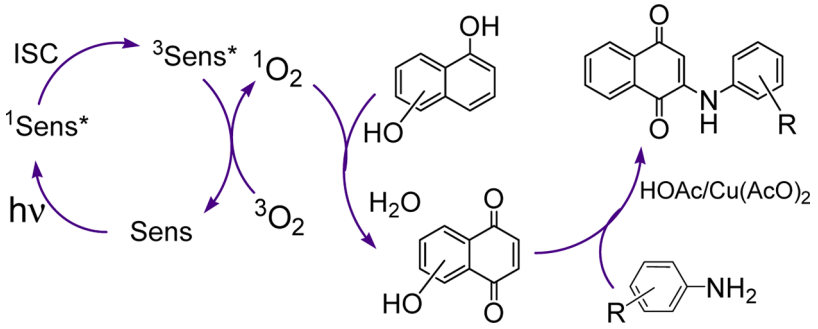
Scheme 3. Proposed One-pot Reaction Mechanism for the Photooxidation with the Triplet Photosensitizers B-1, B-4, or TPP



anticancer reagents.[20] The reactions catalyzed with other organic triplet photosensitizers show similar results (see Supporting Information).

The reaction mechanism for the aerobatic photooxidation of the naphthol with the organic triplet photosensitizers can be summarized in Scheme 3. Singlet oxygen ($^1O_2$) was produced by photosensitizing of the ground state $^3O_2$ by the organic triplet photosensitizers. Then the naphthol was oxidized by the $^1O_2$. The addition of the aromatic amines to the naphthalquinones leads to the production of the functionalized aminonaphthoquinones. Our strategy offers a useful approach to prepare the bioactive aminonaphthoquinones.[20]

2.5. Conclusions. In summary, we used iodo-Bodipy derivatives as organic photocatalysts for two different photoredox organic reactions. These new organic photocatalysts show strong absorption of visible light, efficient triplet state production, and a long-lived triplet excited state. All of these properties are crucial for photoredox catalytic organic reactions because strong absorption of visible light and efficient production of the triplet state will make the activated catalysts more abundant. On the other hand, the long-lived triplet excited state of the photocatalysts will ensure effcient single electron transfer (SET) between the photocatalyst and the substrate molecules. Herein, with the new organic photocatalysts, we investigated two different photocatalytic reactions, that is, the aerobic photocatalysis oxidative coupling of amines (to produce imines with formation of C−N bond), and the photocatalytic singlet oxygen ($^1O_2$) mediated photooxidation of dihydroxylnaphthalenes, and thereafter the C−H functionalization of 1,4-naphthoquinone to produce *N*-aryl-2-amino-1,4-naphthoquinones (one-pot reaction), which are anticancer and antibiotic reagents. Greatly accelerated photoreactions were found for all the reactions compared to that catalyzed with the conventional Ru(II)/Ir(III) complexes, which show weak absorption in the visible region and short-lived triplet excited states. Currently most of the triplet photosensitizers used for the photoredox reactions are the off-the-shelf known triplet photosensitizers, such as Ru(II) polyimine complexes or Eosin Y. Our result will inspire the designing of new organic triplet photosensitizers that show strong absorption of visible light and long-lived triplet excited states and the application of these new organic photocatalysts in photoredox catalytic organic reactions.

3. EXPERIMENTAL SECTION

3.1. General Methods. Compounds **B-1** and **B-2** were prepared following the reported methods.[26]

3.2. B-3. 1 (57.0 mg, 0.1 mmol) and phenylacetylene (11.0 mg 0.1 mmol) were dissolved in THF/Triethylamine (20 mL, v/v = 1:1). Ar was bubbled through the solution for 30 min, then $Pd(PPh_3)_2Cl_2$ (0.005 mmol, 3.5 mg), CuI (0.01 mmol, 2.0 mg) was added. The mixture was refluxed for 4 h under an argon atmosphere. After removal of the solvent under reduced pressure, the mixture was purified by column chromatography (Silica gel, CH_2Cl_2/hexanes, 1/2, v/v) to give a deep-red solid. Yield: 20 mg (35%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.57−7.55 (m, 3H), 7.50−7.47 (m, 2H), 7.36−7.34 (m, 3H), 7.32−7.31 (m, 2H), 2.75 (s, 3H), 2.70 (s, 3H), 1.54 (s, 3H), 1.52 ppm (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.8, 156.7, 145.0, 142.1, 134.8, 132.0, 131.5, 129.6, 129.5, 128.3, 127.9, 123.5, 96.7, 94.6, 85.6, 81.6, 17.0, 16.1, 13.9, 13.6 ppm. MALDI-HRMS calcd $[C_{27}H_{22}BF_2N_2I]^+$ *m*/*z* 550.0889; found *m*/*z* 550.0867.

3.3. B-4. B-1 (57.0 mg 0.1 mmol) was dissolved in dry DMF (5 mL). Benzaldehyde (42.0 mg 0.4 mmol) was added, followed by acetic acid (3 drops) and piperidine (3 drops). The mixture was argon saturated before it was subjected to microwave irradiation (12 min, 150 °C, 1 min prestirring). After removal of the solvent under reduced pressure, the mixture was purified by column chromatography (Silica gel, CH_2Cl_2) to give a deep-purple solid. Yield: 30.0 mg (42%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18−8.14 (d, *J* = 16.0 Hz, 2H), 7.73 (s, 1H), 7.69−7.66 (m, 5H), 7.55−7.52 (m, 3H), 7.44−7.41 (m, 4H), 7.37−7.33 (d, *J* = 16.0 Hz, 2H), 7.31−7.29 (m, 2H), 1.46 ppm (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.8, 150.8, 146.3, 139.9, 139.7, 136.8, 133.1, 129.0, 128.9, 128.5, 128.3, 128.0, 127.8, 19.5, 118.9, 29.9 ppm. MALDI-HRMS calcd $[C_{33}H_{25}BF_2N_2I_2]^+$ *m*/*z* 752.0168, found *m*/*z* 752.0171.

3.4. Typical Procedures for Photocatalytic Oxidative Coupling of Amines. To a dry 10 mL flask were added triplet photosensitizer (0.005 mmol, 1.0 mol %, as the photocatalyst), benzylamine (52 μL, 0.5 mmol) (or other benzylamine derivatives) and acetonitrile (5 mL). The reaction mixture was stirred at 22 °C under air atmosphere. The solution was then irradiated using a 35 W xenon lamp through a cut off filter (0.72 M $NaNO_2$ aqueous solution, which is transparent for light >385 nm). Thin layer chromatography (TLC) was used to monitor the progress of the reaction. After the reaction is completed, the solvent was evaporated under reduced pressure. The residue was directly used in the ^{1}H NMR spectral study and the conversion yields were calculated by integrating the proton peaks. The conversion of the reaction was calculated by integrating the singlet peak of the featured proton in the products (at about 4.87 ppm for −CH═N−C***H***$_2$-) and that of the corresponding proton in the starting materials (at about 3.98 ppm as singlet for NH_2-C***H***$_2$-) in the ^{1}H NMR spectrum.

3.5. Typical Procedures for Photooxidation of Naphthols to Produce Naphthoquinone. To a dry 10 mL flask were added triplet photosensitizer (0.010 mmol 2 mol %), naphthol (0.5 mmol) (or other naphthol derivatives) and $CHCl_3$/methanol (10 mL, v/v, 4:1). The reaction mixture was stirred at 22 °C under air atmosphere. The solution was then irradiated using a 35 W xenon lamp through a cut off filter (0.72 M $NaNO_2$ aqueous solution, which is transparent for light >385 nm). Thin layer chromatography (TLC) was used to monitor the progress of the reaction. After the reaction is completed, the solvent was evaporated under reduced pressure. The mixture was purified by column chromatography (silica gel, CH_2Cl_2).

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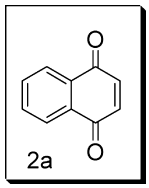
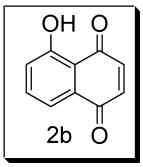
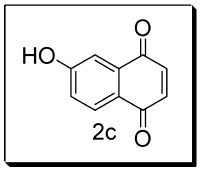


2a. Yield: 74% (58.5 mg), ^{1}H NMR (400 MHz, $CDCl_3/CD_3OD$): δ ppm 8.11−8.08 (m, 2 H), 7.82−7.79 (m, 2H), 7.01 (s, 2H). TOF HRMS EI$^+$: Calcd $[C_{10}H_6O_2]^+$ m/z 158.0368, found m/z 158.0367.

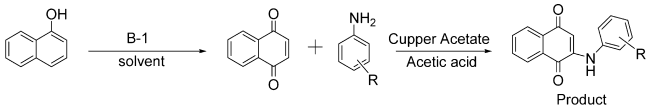


2b. Yield: 73% (63.5 mg), ^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6): δ ppm 11.86 (s, 1H); 7.70 (t, J = 7.6 Hz, 1H); 7.61 (d, J = 8.4 Hz, 1H); 7.56 (d, J = 7.6 Hz, 1H); 7.31 (d, J = 8.4 Hz, 1H); 7.17 (t, J = 8.0 Hz, 1H). TOF HRMS EI$^+$: Calcd $[C_{10}H_6O_3]^+$ m/z 174.0317, found m/z 174.0314.

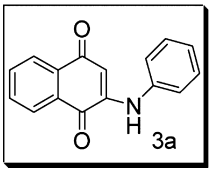


2c. Yield: 80% (69.6 mg), ^{1}H NMR (400 MHz, $CDCl_3/CD_3OD$): δ ppm 7.97 (d, J = 8.0 Hz, 1H), 7.41(s, 1H), 7.16 (d, J = 8.0 Hz, 2 H), 6.91 (s, 2H). TOF HRMS EI$^+$: Calcd $[C_{10}H_6O_3]^+$ m/z 174.0317, found m/z 174.0315.

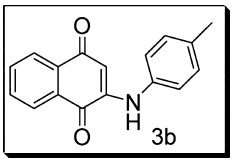
3.6. Typical Procedures for One-pot Synthesis of Naphthoquinone Derivatives. To a dry 10 mL flask were added **B-1**



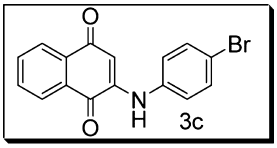
(0.025 mmol 5 mol %), naphthol (0.5 mmol), and $CHCl_3$/methanol (10 mL, v/v, 4:1) cosolvent. The reaction mixture was stirred at 22 °C under air atmosphere. The solution was then photoirradiated using a 35 W xenon lamp for 0.5 h through a cut off filter (0.72 M $NaNO_2$ aqueous solution, which is transparent for light >385 nm). Thin layer chromatography (TLC) was used to monitor the reaction; after the consumption of naphthol, the photoirradiation was stopped, acetic acid (10 mL) was added as well as cupper acetate (0.050 mmol 10 mol %) and 1.2 equiv of aniline derivatives. The reaction mixture was stirred at 65 °C for 3 h under air atmosphere. After the reaction was completed, the solvent was evaporated under reduced pressure. The residual was purified by column chromatography (silica gel, CH_2Cl_2/CH_3OH 50/1, v/v).



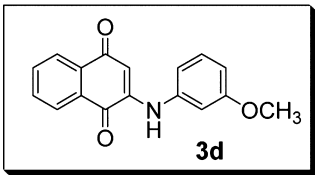
3a. Yield: 70% (87.2 mg), ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.11 (t, J = 6.12 Hz, 2H), 7.76 (t, J = 7.2 Hz, 2H), 7.67 (t, J = 8.0 Hz, 2H), 7.57 (s, 1H), 7.42 (t, J = 7.64 Hz, 2H), 7.22 (t, J = 6.14 Hz, 1H), 6.42 (s, 1H). TOF HRMS EI$^+$: Calcd $[C_{16}H_{11}NO_2]^+$ m/z 249.0797, found m/z 249.0790.



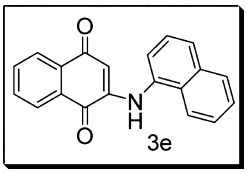
3b. Yield: 71% (93.4 mg), ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.12 (d, J = 7.6 Hz, 2H), 7.75 (t, J = 6.2 Hz, 1H), 7.66 (t, J = 7.6 Hz, 1H), 7.49 (s, 1H), 7.48−7.42 (m, 2H), 7.21−7.14 (m, 2H), 6.36 (s, 1H), 2.36 (s, 3H). TOF HRMS EI$^+$: Calcd $[C_{17}H_{13}NO_2]^+$ m/z 263.0946, found m/z 263.0956.



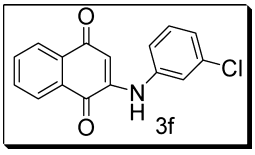
3c. Yield: 48% (78.2 mg), ^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6/Acetone-d_6): δ ppm 8.22 (d, J = 7.6 Hz, 1H), 7.98 (s, 1H), 7.78 (d, J = 7.6 Hz, 1H), 7.46−7.40 (m, 2H), 7.31−7.24 (m, 2H), 7.15 (d, J = 8.8 Hz, 1H), 6.91 (d, J = 7.2 Hz, 1H), 6.65−6.59 (m, 1H). TOF HRMS EI$^+$: Calcd $[C_{16}H_{10}BrNO_2]^+$ m/z 326.9895, found m/z 326.9900.



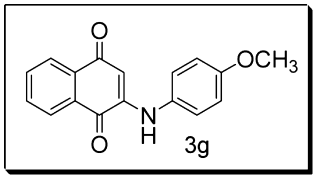
3d. Yield: 74% (103.2 mg), ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.11 (t, J = 4.4 Hz, 2H); 7.76 (t, J = 8.0 Hz, 1H); 7.67 (t, J = 7.6 Hz, 1H); 7.55 (s, 1H); 7.32 (t, J = 8.0 Hz, 1H); 6.88 (d, J = 7.2 Hz, 1H); 6.81 (s, 1H); 6.77 (d, J = 8.4 Hz, 1H); 6.45 (s, 1H); 3.82 (s, 3H). TOF HRMS EI$^+$: Calcd $[C_{17}H_{13}NO_3]$ m/z 279.0895, found m/z 279.0898.



3e. Yield: 79% (118.1 mg), ^{1}H NMR (400 Hz, $CDCl_3$): δ ppm 8.18 (d, J = 7.6 Hz, 1H), 8.10 (d, J = 7.8 Hz, 1H), 7.92−1.90 (m, 2H), 7.82−7.76 (m, 3H), 7.71−7.67 (m, 1H), 7.56−7.53 (m, 3H), 7.50−7.44 (m, 1H), 6.01 (s, 1H). TOF HRMS EI$^+$: Calcd $[C_{20}H_{13}NO_2]$ m/z 299.0946, found m/z 299.0950.



3f. Yield: 77% (108.9 mg), ^{1}HNMR (400 MHz, $CDCl_3$): δ ppm 8.12 (t, J = 6.0 Hz, 2H), 7.77 (t, J = 7.2 Hz, 1H), 7.68 (t, J = 7.6 Hz, 1H), 7.55 (s, 1H), 7.35 (t, J = 8.0 Hz, 2H), 7.29 (s, 1H), 7.18 (t, J = 7.6 Hz, 1H), 6.43 (s, 1H). TOF HRMS EI$^+$: Calcd $[C_{16}H_{10}ClNO_2]^+$ m/z 283.0400, Found m/z 283.0401.



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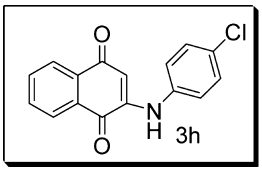
3g. Yield: 73% (101.8 mg), ^{1}HNMR (400 MHz, $CDCl_3$): δ ppm 8.11 (t, J = 6.8 Hz, 2H), 7.75 (t, J = 8.0 Hz, 2H), 7.44 (s, 1H), 7.21 (d, J = 8.8 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 6.22 (s, 1H), 3.83 (s, 3H). TOF HRMS EI$^+$: Calcd $[C_{17}H_{13}NO_3]^+$ m/z 279.0895, found m/z 279.0903.



3h. Yield: 70% (99.1 mg), ^{1}HNMR (400 MHz, $CDCl_3$): δ ppm 8.12 (t, J = 7.2 Hz, 2H), 7.77 (t, J = 8.0 Hz, 1H), 7.68 (t, J = 7.6 Hz, 1H), 7.51 (s, 1H), 7.40 (d, J = 7.6 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 6.36 (s, 1H). TOF HRMS EI$^+$: Calcd $[C_{16}H_{10}ClNO_2]$ m/z 283.0400, found m/z 283.0407.

3.7. Singlet Oxygen ($^1O_2$) Quantum Yields. The $^1O_2$ quantum yields (Φ_Δ) of the photosensitizers were calculated with Rose Bengal (RB) at standard (Φ_Δ = 0.80 in CH_3OH). The absorbance of the $^1O_2$ scavenger 1,3-diphenylisobenzofuran (DPBF) was adjusted around 1.0 in aerated dichloromethane. Then, the photosensitizer was added to cuvette and the absorbance of photosensitizer was adjusted around 0.2−0.3. The cuvette was irradiated with monochromatic light at the peak absorption wavelength of the photosensitizer for 10 s. Absorbance was measured for several times after each irradiation. The slope of absorbance maxima of DPBF at 414 nm versus time graph for each photosensitizer were calculated. Singlet oxygen quantum yield (Φ_Δ) were calculated according to a modified eq 1:[28]

$$\phi(\text{bod}) = \phi(\text{ref}) \times \frac{k(\text{bod})}{k(\text{ref})} \times \frac{F(\text{ref})}{F(\text{bod})} \quad (1)$$

where "bod" and "ref" designate the photosensitizers and "RB", respectively. k is the slope of the plot of absorbance of DPBF (414 nm) against the irradiation time, F is the absorption correction factor, which is given by $F = 1-10^{-OD}$ (OD is the optical density at the irradiation wavelength).

3.8. ESR Spectra. Samples were quantitatively injected into quartz capillaries for ESR analysis in the dark. The illumination was carried out in the sample chamber of the ESR spectrometer. Triplet photosensitizers and superoxide radical anion ($O_2^{-\bullet}$) scavengers (5,5-dimethyl-1-pyrroline-*N*-oxide, DMPO), or singlet oxygen ($^1O_2$) scavengers (2,2,6,6-tetramethylpiperidine, TEMP) in air-saturated CH_3CN was stirred under darkness. Then the solution was injected into the quartz capillary. The quartz capillary was irradiated with laser for 20 s. Then the electron spin resonance (ESR) spectroscopy was studied. A diode pumped solid state (DPSS) continuous laser (532 nm) was used for the irradiation for **B-1**. For **B-4** the laser wavelength is 635 nm.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Molecular structure characterization and additional photocatalysis data. 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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