

Article

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

Ling Huang, Jianzhang Zhao, Song Guo, Caishun Zhang, and Jie Ma

J. Org. Chem., Just Accepted Manuscript • DOI: 10.1021/jo400769u • Publication Date (Web): 13 May 2013 Downloaded from http://pubs.acs.org on May 17, 2013

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.



The Journal of Organic Chemistry is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

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

Ling Huang, Jianzhang Zhao, * Song Guo, Caishun Zhang and Jie Ma

State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of

Technology, Dalian 116024 (China)

E-mail: zhaojzh@dlut.edu.cn; Group homepage: http://finechem.dlut.edu.cn/photochem

RECEIVED DATE (to be automatically inserted)

Table of Contents



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 show weak absorption in visible region and short triplet excited state lifetime. Herein the organic catalysts are used for two photocatalyzed reactions mediated by singlet oxygen $(^{1}O_{2})$, i.e. 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 (onepot reaction), which are anti-cancer 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 result will inspire the design and application of new organic triplet photosensitizers which show strong absorption of visible light and long-lived triplet excited state, and for the application of these catalysts in photoredox catalytic organic reactions.

Keywords: aerobic oxidative coupling; bodipy; photochemistry; triplet photosensitizer; visible light; photoredox catalysis

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 (H₂) 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[PF₆]₂ (bpy = 2,2'-bipyridine) or Ir(ppy)₃ complex (ppy = 2-phenylpyridine),¹⁴ or

Page 3 of 30

The Journal of Organic Chemistry

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,1g} Recently, Eosin Y was used for intermolecular α -alkylation of aldehydes and direct C–H arylation of heteroarenes with aryl diazonium salts,¹⁵ 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 are 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 are below 450 nm. Triplet photosensitizers with absorption in 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 which 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 oranic reaction was carried out with organic photocatalyts that show strong absorption in visible region and readily changeable molecular structures.^{2,8,18}

The *organic* photosensitizers for photocatalysis should be with the following properties, (1) strong absorption of visible light, preferably in green and red region of the spectrum; (2) with triplet excited state 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.

In order to address the above challenges, herein we prepared a series of iodo-Bodipy as triplet photosensitizers which 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* type 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 anti-cancer 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.

2.1. 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, heavy atom 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.

Scheme 1. Synthesis of B-3 and B-4. The known compounds B-1, B-2, TPP, Ru-1, Ir1 and Rose Bengal were presented "



^a Key: (a) Pd(PPh₃)₂Cl₂, CuI. Yield 35%. (b) piperidine, AcOH, DMF, microwave. Yield: 42%.

2. RESULTS AND DISCUSSIONS

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(bpy)₃[PF₆]₂, moderate absorption in the visible range were observed ($\varepsilon = 16700 \text{ M}^{-1} \text{ cm}^{-1}$ at 451 nm). For the Bodipy-based organic photocatalysts **B-1-B-4**, however, much more intense absorption at red-shifted range were observed, the molar absorption coefficients are up to 89000 M⁻¹ cm⁻¹ in the range of 511 nm – 630 nm. The lifetimes of the triplet excited states were determined as 1.8 µs – 84.6 µs (Table 1).The photophysical properties of the triplet photosensitizers (the photocatalysts) were compiled in Table 1.



Figure 1. (a) UV–vis absorption spectra of (a) B-1–B-4 and (b) TPP, Ru-1 and RB. In CH₃CN, $(1.0 \times 10^{-5} \text{ M}; 22 \text{ °C}).$

Notebly B-4 shows a short triplet excited state lifetime (1.8 μ s), but the singlet oxygen quantum yield ($\Phi_{\Delta} = 0.69$) is comparable to that of **B-1** (Table 1). The most probable reason is that the lifetime of **B-4** (1.8 μ s) is already long enough to efficiently produce singlet oxygen ($^{1}O_{2}$) 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 which are with different triplet state lifetime. Similar results were observed

The Journal of Organic Chemistry

previously. For example, $Ir(ppy)_2(bpy)$ complex is with short-lived triplet excited state (0.34 µs), but the ${}^{1}O_2$ quantum yield is high ($\Phi_{\Delta} = 0.97$).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).

Table 1. Photophysical parameters of the photocatalysts (triplet photosensitizers)^a

	λ_{abs} / nm	e ^[b]	$\lambda_{ m em}$ / nm	$\pmb{\Phi}_F/\%^{[c]}$	$oldsymbol{ au}$ / $\mu s^{[d]}$	$\Phi_{\Delta}/\%^{[e]}$
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
ТРР	411	3.08	655	10.0	70.0	0.62
Ru-1	451	0.167	607	6.1	0.45	0.57

^{*a*} In CH₃CN (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 ($\Phi = 0.72$ in THF). ^{*d*} Triplet state lifetimes, measured by transient absorption spectra, in μ s. ^{*e*} Singlet oxygen quantum yield. With Rose Bengal (RB) as the standard ($\Phi_{\Delta} = 0.8$ In Methanol). 22 °C.

2.3. Photocatalytic oxidative coupling of amines. Firstly the iodo-Bodipy triplet photosensitizers were used for oxidative coupling of amines. Recently inorganic material of carbon nitride and prophyrin derivatives were 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 O₂. 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 blue region and the reaction was carried out under neat O₂ and 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.

Table 2. Transformation of benzylamine catalyzed by different triplet photosensitizers ^a

Entry	photosensitizer	solvent	T [°C]	<i>t</i> [h]	Conv. [%] ^{bc}
1	Rose Bengal	acetonitrile	20	1 h	81
2	B-1	acetonitrile	20	1 h	100
3	B-2	acetonitrile	20	1 h	100
4	B-3	acetonitrile	20	1 h	100
5	B-4	MeCN/CH ₂ Cl ₂ (3.2 v/v)	25	1 h	100
7	TPP	acetonitrile	20	1 h	11
8	TPP	CH_2Cl_2	20	1 h	57
9	Ru(bpy) ₃	acetonitrile	25	1 h	58
7	Ir(ppy) ₂ bpy	acetonitrile	20	1 h	37

^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 The reaction was monitored by TLC. Only two spots were found (except
photosensitizer), therefore the selectivity of the photoreaction is good.

NH ₂	\rightarrow		N N
*		\sim	~

The Journal of Organic Chemistry

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-C₃N₄.⁸ For example, the reaction can be run in aerated solution (not neat O₂ 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-C₃N₄ as the photosensitizer, the same reaction has to be run at 5 atm neat O₂ atmosphere (not air), elevated temperature (80 °C) and with prolonged reaction time (2–5 hr).⁸ Furthermore, we found that the typical off-the-shelf organic triplet photosensitizers, such as TPP, Rose Bengal (RB), [Ir(ppy)₂(bpy)]PF₆ 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).

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, 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







Entry	Substrate	Product	<i>t</i> [h]	Yield% ^b	TON ^d	$TOF / min^{-1}e$
1	NH ₂	N V	1.0	100	100	1.6
2	F NH ₂	F	0.5	60	60	1.0
3	N N		1.0	91	91	1.5
4	NH ₂		1.0	100	100	1.6
5	NH ₂		1.0	89	89	1.5
6	NH ₂		1.0	100	100	1.7
7	CI NH2		1.0	100	100	1.7
8	F NH2		2.0	44	44	0.4
9	F ₃ C	F ₃ C	2.0	66	66	0.6
10	NH	N	2.5	74	74	1.2
11	N OH H	N OH	2.5	62	62	0.4
12 ^f	N H		4.0	100	100	0.4
13 ^f	N H	N	4.0	100	100	0.4
14	NH ₂	N=N-	3.0	_ c	_	-

^{*a*} Reaction conditions: benzylamir mol%), solvent (5 mL), in air, $\lambda > 3$ with ¹H NMR. ^{*c*} No reaction. ^{*d*} T product/moles of catalyst. ^{*e*} Turnove mW/cm². results. ^{1f} We propose that the interme absraction by ¹O₂) is more stable than was produced for the asymmetrical a donating substituents give higher y substituents (Entry 2, 7-9, Table 3). T carried out (see Supporting Information up to 95 % was obtained (Supporting The experiments indicated that ox are all essential for the photocatalytic

^{*a*} Reaction conditions: benzylamine (0.5 mmol), photosensitizers catalyst (0.005 mmol, 1 mol%), solvent (5 mL), in air, $\lambda > 380$ nm (20 mW/cm²), 1 h, 22 °C. ^{*b*} Yield was determined with ¹H NMR. ^{*c*} No reaction. ^{*d*} Turnover number, calculated by the ratio of moles of product/moles of catalyst. ^{*e*} Turnover frequency. ^{*f*} The photoirradiation power density is 37 mW/cm².

results.^{1f} We propose that the intermediated at the aryl side (such as radical, due to the hydrogen absraction by ${}^{1}O_{2}$) 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 benzylamine with electrodonating substituents give higher yields than the benzylamines with electron-withdrawing substituents (Entry 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).

The experiments indicated that oxygen (O₂), 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 ${}^{1}O_{2}$ scavenger. In the presence of superoxide dismutase (SOD), however, the photooxidation proceeded as normal. Therefore we propose that presence of ${}^{1}O_{2}$ 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 nanosecond transient absorption spectra, 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 ${}^{1}O_2$, respectively.⁹

Table 4. Mechanism study of the oxidation amines experiments using B-1. The general reaction is applicable to entries 1-6^{*a*}

	NH ₂ –]
Entry	Condition	solvent	<i>t</i> / [h]	Yield[%] ^b
1	In air	acetonitrile	1	99
2	In N ₂	acetonitrile	3	_ <i>c</i>
3	No photoirradiation	acetonitrile	3	_ <i>c</i>
4	No B-1	acetonitrile	3	4
5	3 eqv TFA	CH_2Cl_2	3	_ <i>c</i>
6	2,6-di-tert-butylmethylphenol	acetonitrile	1	70
	(0.05 mmol)			
7	2 eqv. Histidine	THF/H ₂ O=1/2	1	9
8	No histidine	THF/H ₂ O=1/2	1	80
9	SOD (2 eqv.) d	acetonitrile	1	100

^a 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 $(\lambda > 380 \text{ nm } 20 \text{ mW/cm}^2)$. ^b The yields were determined by ¹H 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 CH₃CN. 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 ${}^{1}O_{2}$ -TEMP adduct was detected upon photoexcitation (Figure 2b). In the presence of benzylamine, however, the magnitude of the signal was greatly attenuated (Figure 2a), indicated that the ${}^{1}O_{2}$ was consumed in the presence of benzylamine, therefore, the oxidative coupling of the benzylamine was mediated by ${}^{1}O_{2}$. With DMPO, however, the signal of the DMPO- $O_{2}^{-\bullet}$ adduct did not change in the presence of benzylamine, indicated that $O_{2}^{-\bullet}$ was not involved in the photocatalytic reaction.

The reaction mechanism of the ${}^{1}O_{2}$ -mediated aerobatic oxidative coupling of the amines can be summarized in Scheme 2.^{1f 1}O₂ was produced by the triplet photosensitizers. Then the amine was oxidized to the imine and hydrogen peroxide (H₂O₂) was produced. Reaction of the imine with another molecule of amines produce the Schiff base product. NH₃ was produced as side

product.^{1f} We studied the photocatalytic reaction in CDCl₃/CHCl₃.^{1f} Previously it was found that the photocatalytic reaction proceeded with higher velocity in deuterated solvents because the lifetime of ¹O₂ is longer in deuterated solvent than in their proteated counterparts.^{1f} We also observed much higher reaction velocity in CDCl₃ than that in CHCl₃ (see Supporting Infomration, Table S7). This result indicated that ¹O₂ is involved in the photocatalytic reactions. Moreover, as a proof of the proposed mechanism, H₂O₂ was detected by using KI/CH₃COOH. Brown color was observed by mixing the photocatalytic reaction mixture and KI/CH₃COOH (see Supporting Information, Figure S90).^{1f} Furthermore, the effect of DABCO (1,4diazabicyclo[2.2.2]octane, a singlet oxygen scanvenger) on the photocatalytic oxidative coupling of benzylamines was also studied. We found that the photocatalytica reaction can be signicicantly surpressed by the DABCO (Supporting Information, Table S8).^{1f} Therefore, ¹O₂ is involved in the photocatalytic reaction. All these results support the proposed mechanism (Scheme 2).

Scheme 2. Proposed reaction mechanism for the photocatalytic aerobatic oxidation of amines with the triplet photosensitizers B-1 - B-4



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 (${}^{1}O_{2}$) can be produced by the triplet photosensitizers in the presence of O_{2} .²⁸⁻³⁵ Therefore the ${}^{1}O_{2}$ -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 to give *N*-aryl-2-amino-1,4-naphthoquinones, which are anti-cancer 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 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 anti-cancer reagents.²⁰



Figure 3. UV-vis absorption spectral changes for the photooxidation of DHN. (a) B-1 as a sensitizer. (b) B-4 as sensitizer (in CH₂Cl₂/MeOH, 9:1, v/v). c[sensitizers] = 1.0 × 10⁻⁵ M. c[DHN] = 1.0 × 10⁻⁴ M. Light intensity: 20 mW/cm², 20 °C.

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 produces, the photooxidation of DHN was coupled to the adduction of aromatic amines into a one-pot reaction (Table 6).⁴⁰

	HO I	OH B-1/ Visible Air	B-4 Light HO rt HO		
Entry	Substrate 1	Product 2	Yield ^b	TON ^c	TOF/ min ^{-1 d}
1	OH 1a		74/81	37/40	0.6/0.7
2	OH OH OH 1b	OH O 2b O	73/77	36/38	0.6/0.6
3	HO 1c		80/87	40/43	0.7/0.7

Table 5.	Photooxidation	of naphthol	with B-1	and B-4 ^a
I abit 5.	1 IIUUUAIualiuli	or naphtnor		anu D- T

^{*a*} Reaction conditions: substrate **1** (0.10 mmol), photocatalyst **B-1/B-4** (2 mol%), in CH₂Cl₂/CH₃OH(v/v, 4:1, 5.0 mL). The reaction mixture was irradiated with 35 W Xe lamp for 30 min (0.72 M NaNO₂ solution was used as filter so that light with wavelength $\lambda < 385$ nm was blocked. The light intensity at the photoreactor is 20 mW/cm²). 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.

In the first step of the reaction, the naphthol was oxidized to naphthoquinones. Then without isolation, aromatic amines and Cu^{2+} saltswere added, the adduction products aminonaphthoquinones were obtained.²⁰ The one-pot reaction was optimized with TPP as the



^a Step 1: Naphthol (0.5 mmol) and photosensitizer **B-1** (5mol%) were mixed in CHCl₃/Methanol (10 mL, 4/1, v/v). The mixture was irradiated with 35W Xe lamp (λ >385 nm. 30 mW/cm²) 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.

 triplet photosensitizer (Supporting Information, Table S6). The result shows that the optimal reaction conditions for the one-pot preparation of aminonaphthoquinones are 1.5 h for the first step, 3 h reaction time for the second step of the one-pot reaction. The reactions were carried out at 65 °C. The reaction is tolerant to aromatic amines substrates with various functional groups (see Supporting Information for the substrate tolerance study). However, 4-nitroaniline failed to produce the aminonaphthoquinone (Figure S5). Furthermore, we found that CuSO₄ 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 visible region. These results are promising for preparation of anti-cancer reagents.²⁰ The reactions catalyzed with other organic triplet photosensitizers show similar results (see Supporting Information).

Scheme 3. Proposed one pot reaction mechanism for the photooxidation with the triplet photosensitizers **B-1**, **B-4** or TPP



The reaction mechanism for the aerobatic photooxidation of the naphthol with the organic triplet photosensitizers can be summarized in Scheme 3. Singlet oxygen (${}^{1}O_{2}$) was produced by photosensitizing of the ground state ${}^{3}O_{2}$ by the organic triplet photosensitizers. Then the naphthol

Page 19 of 30

The Journal of Organic Chemistry

was oxidized by the ${}^{1}O_{2}$. 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 long-lived triplet excited state. All these properties are crucial for photoredox catalytic organic reactions because strong absorption of visible light and efficient production of 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, i.e. the aerobic photocatalysis oxidative coupling of amines (to produce imines with formation of C–N bond), and the photocatalytic singlet oxygen $(^{1}O_{2})$ 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 anti-cancer 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 which show strong absorption of visible light and long-lived triplet excited states, and for the application of these new organic photocatalysts in photoredox catalytic organic reactions.

 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) was dissolved in THF/Triethylamine (20 mL, v/v = 1:1). Ar was bubbled through the solution for 30 min, then Pd(PPh₃)₂Cl₂ (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. CH₂Cl₂/hexanes, 1/2, v/v) to give deep red solid. Yield: 20 mg (35%). ¹H NMR (400 MHz, CDCl₃) δ = 7.57–7.55 (m, 3 H), 7.50–7.47 (m, 2 H), 7.36–7.34 (m, 3H), 7.32–7.31 (m, 2 H), 2.75 (s, 3 H), 2.70 (s, 3 H), 1.54 (s, 3H), 1.52 ppm (s, 3H). ¹³C NMR (100 MHz, CDCl₃) 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 [C₂₇H₂₂BF₂N₂I]⁺ *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. CH₂Cl₂) to give deep purple solid. Yield: 30.0 mg (42%). ¹H NMR (400 MHz, CDCl₃): 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). ¹³C NMR (100 MHz, CDCl₃): 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 [C₃₃H₂₅BF₂N₂l₂]⁺ *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 μ L, 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 NaNO₂ 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 ¹H NMR spectral study and the conversion yields were calculated by integrating the proton peaks. The conversion of the reaction was calculated by integrating 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 NH₂-C*H*₂-) in the ¹H 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 CHCl₃/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 NaNO₂ 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, CH₂Cl₂).



2a. Yield: 74 % (58.5 mg), ¹H NMR (400 MHz, CDCl₃/ CD₃OD): δ ppm 8.11– 8.08 (m, 2 H), 7.82–7.79 (m, 2H), 7.01 (s, 2H). TOF HRMS EI⁺: Calcd [C₁₀H₆O₂]⁺

HO

2b. Yield: 73 % (63.5 mg), ¹H NMR (400 MHz, CDCl₃/DMSO-d₆):
$$\delta$$
 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.



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 CHCl₃/methanol (10 mL, v/v, 4:1) co-solvent. 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 NaNO₂ 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, cupper acetate (0.050 mmol 10 mol%) and 1.2 eqv. aniline derivatives. The reaction mixture was stirred at 65 °C for 3 h under air atmosphere. After the reaction is completed, the solvent was evaporated under reduced pressure. The residual was purified by column chromatography (silica gel, CH₂Cl₂/CH₃OH 50/1, v/v).

The Journal of Organic Chemistry

3a. Yield: 70 % (87.2 mg), ¹HNMR (400 MHz, CDCl₃):
$$\delta$$
 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), ¹HNMR (400 MHz, CDCl₃): 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), ¹HNMR (400 MHz, CDCl₃/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), ¹HNMR (400 MHz, CDCl₃): 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 [C₁₇H₁₃NO₃] m/z279.0895, found *m*/*z* 279.0898.



3e. Yield: 79 % (118.1 mg), ¹HNMR (400Hz, CDCl₃): 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), ¹HNMR (400 MHz, CDCl₃): 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 $[C_{16}H_{10}CINO_2]^+ m/z$ 283.0400, Found m/z 283.0401.



3g. Yield: 73 % (101.8 mg), ¹HNMR (400 MHz, CDCl₃): 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.



HRMS EI⁺: Calcd [C₁₆H₁₀ClNO₂] m/z 283.0400, found m/z 283.0407.

3.7. Singlet oxygen (${}^{1}O_{2}$) quantum yields. The ${}^{1}O_{2}$ quantum yields (Φ_{Δ}) of the photosensitizers were calculated with Rose Bengal (RB) at standard ($\Phi_{\Delta} = 0.80$ in CH₃OH). The absorbance of the ${}^{1}O_{2}$ 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 seconds. 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 equation (1): 28

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

The Journal of Organic Chemistry

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 $F = 1-10^{-\text{OD}}$ (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 ($^{1}O_{2}$) scavengers (2,2,6,6-tetramethylpiperidine, TEMP) in air-saturated CH₃CN was stirred under darkness. Then the solution was injected into the quartz capillary. The quartz capillary was irradiated with laser for 20 seconds. Then the electron spin resonance (ESR) spectroscopy was studied. A diode pumped solid state (DPSS) continous laser (532 nm) was used for the irradiation for **B-1**, For **B-4** the laser wavelength is 635 nm.

ACKNOWLEDGMENT

We thank the NSFC (20972024, 21073028 and 21273028), the Royal Society (UK) and NSFC (China-UK Cost-Share Science Networks, 21011130154), Ministry of Education (NCET-08-0077 and SRFDP-20120041130005) and Dalian University of Technology for financial support.

S Supporting information

Molecular structure characterization and additional photocatalysis data. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES

(1) (a) Yamaguchi, K.; Mizuno, N. Angew. Chem. Int . Ed. 2003, 42, 1480–1483. (b) Tung, C.
H.; Wu, L. Z.; Zhang, L. P.; Chen, P. Acc. Chem. Res. 2003, 36, 39–47. (c) Xi, Y.; Yi, H.; Lei,

A. Org. Biomol. Chem. 2013, 11, 2387–2403. (d) Hari, D. P.; König, B. Angew. Chem. Int. Ed.
2013, 52, 4734 – 4743. (e) Mitkina, T.; Stanglmair, C.; Setzer, W.; Gruber, M.; Kischc, H.;
König, B. Org. Biomol. Chem. 2012, 10, 3556–3561. (f) Berlicka, A.; and König, B. Photochem.
Photobiol. Sci. 2010, 9, 1359–1366. (g) Füldner, S.; Mitkina, T.; Trottmann, T.; Frimberger,
A.; Gruber, M.; König, B. Photochem. Photobiol. Sci. 2011, 10, 623–625. (h) Lechner, R.;
Kümmel, S.; König, B. Photochem. Photobiol. Sci. 2010, 9, 1367–1377. (i) Füldner, S.; Pohla,
P.; Bartling, H.; Dankesreiter, S.; Stadler, R.; Gruber, M.; Pfitzner, A.; König, B.; Green Chem.

(2) (a) Shi, L.; Xia, W.; Chem. Soc. Rev. 2012, 41, 7687–7697. (b) Xuan, J.; Xiao, W.-J.;
Angew. Chem. Int. Ed. 2012, 51, 6828–6838. (c) Ravelli, D.; Fagnoni, M.; Albini, A. Chem.
Soc. Rev. 2013, 42, 97–113. (d) Zhao, J.; Wu, W.; Sun, J.; Guo, S. Chem. Soc. Rev. 2013, DOI: 10.1039/c3cs35531d.

(3) Oelgemöller, M.; Healy, N.; Oliveira, L.; Jung, C.; Mattay, J. *Green Chem.* **2006**, *8*, 831–834.

(4) (a) Protti, S.; Fagnoni, M.; Photochem. *Photobiol. Sci.* 2009, *8*, 1499–1516. (b) Streb, C. *Dalton Trans.* 2012, *41*, 1651–1659. (c) Zhao, G.; Yang, C.; Guo, L.; Sun, H.; Lin, R.; Xia, W. J. Org. Chem. 2012, *77*, 6302–6306. (d) Wang, Z.-Q.; Hu, M.; Huang, X.-C.; Gong, L.-B.; Xie, Y.-X.; Li, J.-H. J. Org. Chem. 2012, *77*, 8705–8711.

(5) Tucker, J. W.; Stephenson, C. R. J. J. Org. Chem. 2012, 77, 1617–1622.

(6) (a) Cherevatskaya, M.; Neumann, M.; Füldner, S.; Harlander, C.; Kümmel, S.; Dankesreiter, S.; Pfitzner, A.; Zeitler, K.; König, B. *Angew. Chem. Int. Ed.* 2012, *51*, 4062–4066.
(b) Chen, Y.-Z.; Wang, D.-H.; Chen, B.; Zhong, J.-J.; Tung, C.-H.; Wu, L.-Z. *J. Org. Chem.* 2012, *77*, 6773–6777.

The Journal of Organic Chemistry

(7) Condie, A. G.; González-Gómez, J. C.; Stephenson, C. R. J. J. Am. Chem. Soc. 2010, 132, 1464–1465.

(8) (a) Su, F.; Mathew, S..C.; Möhlmann, L.; Antonietti, M.; Wang, X.; Blechert, S. *Angew. Chem. Int. Ed.* 2011, *50*, 657–660. (b) Park, J. H.; Ko, K. C.; Kim, E.; Park, N.; Ko, J. H.; Ryu,
D. H.; Ahn, T. K.; Lee, J. Y.; Son, S. U. *Org. Lett.* 2012, *14*, 5502–5505.

(9) (a) Liu, Q.; Li, Y.N.; Zhang, H. H.; Chen, B.; Tung, C. H.; Wu, L. Z.; *Chem. Eur. J.* 2012, *18*, 620–627; (b) Hecht, S.; Fréchet, J. M. J. *J. Am. Chem. Soc.* 2001, *123*, 6959–6960. (c) Yavorskyy, A.; Shvydkiv, O.; Hoffmann, N.; Nolan, K.; Oelgemöller, M. Org. Lett. 2012, *14*, 4342–4345. (d) Hari, D. P.; Hering, T.; König, B. Org. Lett. 2012, *14*, 5334–5337. (e) Fukuzumi, S.; Ohkubo, K. *Chem. Sci.*, 2013, *4*, 561–574.

(10) Su, F.; Mathew, S. C.; Lipner, G.; Fu, X.; Antonietti, M.; Blechert, S.; Wang, X. J. Am. Chem. Soc. 2010, 132, 16299–16301.

(11) Xu, Y.; Eilers, G.; Borgstrçm, M.; Borgstrçm, J.; Abrahamsson, M.; Magnuson, A.;
Lomoth, R.; Bergquist, J.; Políka, T.; Sun, L.; Sundstrçm, V.; Styring, S.; .Hammarstrçm, L.;
Åkermark, B. *Chem. Eur. J.* 2005, *11*, 7305–7314.

(12) Singh, W. M.; Pegram, D.; Duan, H.; Kalita, D.; Simone, P.; Emmert, G. L.; Zhao, X.*Angew. Chem. Int. Ed.* 2012, *51*, 165–1656.

(13) Fukuzumi, S.; Kobayashi, T.; Suenobu, T.; Angew. Chem. Int. Ed. 2011, 50, 728-731.

(14) (a) Zou, Y. Q.; Lu, L. Q.; Fu, L.; Chang, N. J.; Rong, J.; Chen, J. R.; Xiao, W. J. Angew. *Chem. Int. Ed.* 2011, *50*, 7171–7175. (b) Ye, Y.; Sanford, M. S. *J. Am. Chem. Soc.* 2012, *134*, 9034–9037. (c) Hanson, K.; Ashford, D. L.; Concepcion, J. J.; Binstead, R. A.; Habibi, S.; Luo, H.; Glasson, C. R. K.; Templeton, J. L.; Meyer, T. J. *J. Am. Chem. Soc.* 2012, *134*,

16975–16978. (d) DiRocco, D. A.; Rovis, T. J. Am. Chem. Soc. 2012, 134, 8094–8097. (e)
Amaoka, Y.; Kamijo, S.; Hoshikawa, T.; Inoue, M. J. Org. Chem. 2012, 77, 9959–9969. (f)
Mori, K.; Tottori, M.; Watanabe, K.; Che, M.; Yamashita, H. J. Phys. Chem. C 2011, 115,
21358–21362. (g) Cheng, Y.; Yang, J.; Qu, Y.; Li, P. Org. Lett., 2012, 14, 98–101. (h)
Neumann, M.; Zeitler, K. Org. Lett. 2012, 14, 2658–2661. (i) Hering, T.; Hari, D. P.; König, B.
J. Org. Chem. 2012, 77, 10347–10352.

(15) (a) Neumann, M.; Füldner, S.; König, B.; Zeitler, K.; Angew. Chem. Int. Ed. 2011, 50,

951-954. (b) Hari, D. P.; Schroll, P.; König, B. J. Am. Chem. Soc. 2012, 134, 2958-2961.

(16) Hari, D. P.; König, B. Org. Lett., 2011, 13, 3852-3855.

(17) Pan, Y.; Kee, C. W.; Chen, L.; Tan, C. H. Green Chem. 2011, 13, 2682–2685.

(18) Xuan, J.; Xiao, W. J. Angew. Chem. Int. Ed. 2012, 51, 6828-6838.

(19) Takizawa, S. Y.; Aboshi, R.; Murata, S. Photochem. Photobiol. Sci. 2011, 10, 895–903.

(20) Benites, J.; Valderrama, J. A.; Bettega, K.; Pedrosa, R. C.; Calderon, P. B.; Verrax, J. *Eur. J. Med. Chem.* **2010**, *45*, 6052–6057.

(21) Loudet, A.; Burgess, K. Chem. Rev. 2007, 107, 4891-4932.

(22) Ulrich, G.; Ziessel, R.; Harriman, A. Angew. Chem. Int. Ed. 2008, 47, 1184–1201.

(23) Ziessel, R.; Harriman, A. Chem. Commun., 2011, 47, 611–631.

(24) (a) Yukruk, F.; Dogan, A. L.; Canpinar, H.; Guc, D.; Akkaya, E. U. Org. Lett., 2005, 7, 2885–2887. (b) Zhou, Y.; Xiao, Y.; Chi, S.; Qian, X. Org. Lett., 2008, 10, 633–636. (c) Zhou, Y.; Yoon, J.; Chem. Soc. Rev., 2012, 41, 52–67.

The Journal of Organic Chemistry

3
1
4
5
6
7
8
q
10
10
11
12
13
14
15
16
10
17
18
19
20
21
22
22
23
24
25
26
27
28
20
29
30
31
32
33
34
25
30
30
37
38
39
40
<u>⊿1</u>
40
42
43
44
45
46
47
18
40
49
50
51
52
53
54
55
55
56
57
58
59
60

(25) (a) Yogo, T.; Urano, Y.; Ishitsuka, Y.; Maniwa, F.; Nagano, T. J. Am. Chem. Soc. 2005, 127, 12162–12163. (b) Kamkaew, A.; Lim, S. H.; Lee, H. B.; Kiew, L. V.; Chung, L. Y.; Burgess, K. Chem. Soc. Rev. 2013, 42, 77–88.

(26) Wu, W.; Guo, H.; Wu, W.; Ji, S.; Zhao, J. J. Org. Chem. 2011, 76, 7056-7064.

(27) Chen, Y.; Zhao, J.; Xie, L.; Guo, H.; Li, Q. RSC Adv., 2012, 2, 3942–3953.

(28) Cakmak, Y.; Kolemen, S.; Duman, S.; Dede, Y.; Dolen, Y.; Kilic, B.; Kostereli, Z.; Yildirim, L. T.; Dogan, A. L.; Guc, D.; Akkaya, E. U. *Angew. Chem. Int. Ed.* **2011**, *50*, 11937–11941.

(29) Amin, A, N.; El-Khouly, M. E.; Subbaiyan, N. K.; Zandler, M. E.; Fukuzumi, S.; D'Souza, F. *Chem. Commun.* **2012**, *48*, 206–208.

(30) Liu, F.; Zhao, J. Chem. Commun. 2012, 48, 3751-3753.

(31) Awuah, S. G.; You, Y. RSC Adv., 2012, 2, 11169–11183.

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

(33) Adarsh, N.; Avirah, R. R.; Ramaiah, D. Org. Lett. 2010, 12, 5720-5723.

(34) Duman, S.; Cakmak, Y.; Kolemen, S.; Akkaya, E. U.; Dede, Y. J. Org. Chem. 2012, 77, 4516–4527.

(35) Awuah, S. G.; Polreis, J.; Biradar, V.; You, Y. Org. Lett. 2011, 13, 3884–3887.

(36) Sun, J.; Zhao, J.; Guo, H.; Wu, W. Chem. Commun . 2012, 48, 4169-4171.

(37) Liu, Y.; Zhao, J. Chem. Commun. 2012, 48, 3751-3753.

(38) Yi, X.; Zhao, J.; Sun, J.; Guo, S.; Zhang, H. Dalton Trans. 2012, 42, 2062–2074.

(39) Adarsh, N.; Shanmugasundaram, M.; Avirah, R. R.; Ramaiah, D. *Chem. Eur. J.* **2012**, *18*, 12655–12662.

(40) Lisboa, C. de S.; Santos, V. J.; Vaz, B. G.; de Lucas, N. C.; Eberlin, M. N.; Garden, S. J. J.

Org. Chem. 2011, 76, 5264–5273.