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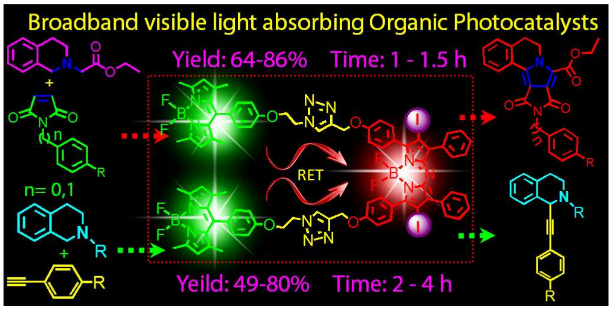
Graphical Abstract:

Photoredox catalytic organic reactions promoted with broadband visible light-absorbing Bodipy-iodo azaBodipy triad photocatalyst

Guo Song, Renjie Tao and Jianzhang Zhao*



Bodipy-diiodo AzaBodipy triad showing broadband visible light-absorption was used as efficient photocatalyst for photoredox catalytic organic reactions.

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ARTICLE

Photoredox catalytic organic reactions promoted with broadband visible light-absorbing Bodipy-iodo azaBodipy triad photocatalyst

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2,6-diiodo-aza-Bodipy (**B-1**) and Bodipy-2,6-diiodo-aza-Bodipy triad (**B-2**) was used as novel photocatalysts for photoredox catalytic organic reactions with tetrahydroisoquiniline as substrates to prepare highly functionalized organic compounds via the [3+2] cycloaddition/aromatization tandem reaction, and the Cu(I) catalyzed alkynylation reactions. Different from the conventional photocatalysts such as $Ru(bpy)_3Cl_2$, Eosin Y or Rose Bengal, which are based on mono-visible light-harvesting chromophore profile and show weak absorption in visible region, the new photocatalysts show strong absorption in visible region (ε = 73000 M^{-1} cm^{-1} at 683 nm, **B-1**). More importantly, resonance energy transfer (RET) was used to enhance the absorption of photocatalyst **B-2** in visible region, in which two Bodipy units were used as energy donor and aza-Bodipy as energy acceptor. **B-2** shows *broadband* absorption in the range 400 nm – 750 nm (ε = 165000 M^{-1} cm^{-1} at 504 nm, and 71000 M^{-1} cm^{-1} at 683 nm). The iodo-Aza Bodipy is more efficient as photocatalyst than the conventional ones such as $[Ru(bpy)_3]Cl_2$. Furthermore, the broadband visible light-absorbing **B-2** is more efficient as photocatalyst than a previously reported monochromophore photocatalyst **B-4** (diiodo-Bodipy). Our results are useful for designing of efficient organic triplet photosensitizers as photocatalyst to improve the photoredox catalytic organic reactions.

Introduction

Photoredox catalytic organic reactions have attracted much attention.[1-8] With this novel synthetic method, highly functionalized organic compounds can be prepared with high yields and good selectivity under mild reaction conditions. It has been proved that a wide variety of reactions can be improved with photocatalytic approach. For example, the reactions with generation of radicals, dehalogation, dehydrogenation coupling and [3+2] cycloadditions, etc.[1-6] However, the photocatalysts used for these photocatalytic organic reactions are limited to the off-the-shelf compounds, such as $Ru(bpy)_3Cl_2$,[2,9-14] and few xathene dyes such as Eosin Y and Rose Bengal.[15-20] These conventional photocatalysts suffer from some disadvantages. For example, $Ru(bpy)_3Cl_2$ gives weak absorption in visible region.[21] For Eosin Y and Rose Bengal, however, it is difficult to modify the molecular structure, as a result the redox potentials of the photocatalysts cannot be readily optimized for different substrates.

On the other hand, organic compounds are with readily derivatizable molecular structures, but organic triplet photosensitizers are rarely reported, because the intersystem crossing (ISC) is usually very weak for neat organic chromophores.[22,23] Furthermore, all the conventional photocatalysts share a same feature, that is, there is only a single kind of light-absorbing unit in the molecules.[23] Hence the excitation energy of a *broadband* light source (white light, such as solar light) cannot be efficiently harvested by these photocatalysts. All these features may diminish the catalytic efficiency. Therefore it is highly desired to design new organic photocatalysts to overcome the aforementioned challenges.

It is useful to have a brief analysis of the mechanisms of the photoredox catalytic organic reactions prior to designing any of triplet photosensitizers as new photocatalysts. Single electron transfer (SET) between the photocatalyst and substrates is the most popular mechanism for the photoredox catalytic reactions.[1,5,24] Owing to the bi-molecular feature of the SET, the following properties of a photocatalyst are crucial,[25] i.e. (a) the light-absorbing ability, (b) the lifetime of the triplet excited states, and (c) the easiness to modify the molecular structure, so that the redox potential of the photocatalyst can be easily tuned to achieve selectivity or to improve the catalytic efficiency. However, it is very difficult, if not impossible, to address these challenges with the conventional photocatalysts such as $Ru(bpy)_3Cl_2$, Eosin Y and Rose Bengal.[1,23]

Herein we used iodo-aza-Bodipy as new photocatalysts to address the above challenges. Importantly, we devised RET triplet photosensitizers which are based on two different chromophores and show broadband absorption in visible region to enhance the light-absorption.[26,27] We found that the organic photocatalysts are efficient for two different bench mark reactions, i.e. the tetrahydroisoquinoline based [3+2] cycloaddition/aromatization tandem reaction,[6,11] and the coupled Cu(I) catalyzed alkynylation of tetrahydroisoquinolines.[28] We proved that the dyad photocatalyst with RET effect is more efficient than the mono-chromophore based photocatalysts. Furthermore, even the mono-chromophore iodo-aza Bodipy photocatalyst demonstrated more efficient photocatalytic efficacy than the conventional photocatalysts such as Ru(bpy)$_3$Cl$_2$. Our results are helpful for designing new organic photocatalysts to improve the photoredox catalytic organic reactions.

Experimental Section

Electron spin resonance (ESR) spectroscopy

ESR Samples were quantitatively injected into quartz capillaries for ESR analysis in the dark and illuminated directly in the cavity of the ESR spectrometer with laser. Organic photocatalysts and 5,5-dimethyl-1-pyrroline-N-oxide (DMPO. Superoxide radical anion $O_2^{\bullet-}$ scavenger), or 2,2,6,6-tetramethylpiperidine (TEMP. Singlet oxygen $^1O_2$ scavengers) in aerated CH$_3$CN was stirred in the dark, then the solution was injected into the quartz capillaries. A diode pumped solid state (DPSS) continuous laser (635 nm) was used for the photoirradiation of the solution in quartz capillaries for 120 seconds.

The general procedure for oxidation/[3+2] cycloaddition/aromatization tandem reaction with tetrahydroisoquinoline derivatives catalyzed by organic triplet photosensitizers B-1 and B-2

Dissolved **1** (0.15 mmol), photosensitizers (1 mmol%) and **2** (0.1 mmol) into dichloromethane (DCM. 5 mL). 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. NBS (25 mg) is added into reactor. Then another 5 min, remove the solvents, The residue was purified by column chromatography (silica gel, DCM).

The general procedure for the photocatalytic aerobic oxidation and metal catalyzed alkynylation reactions

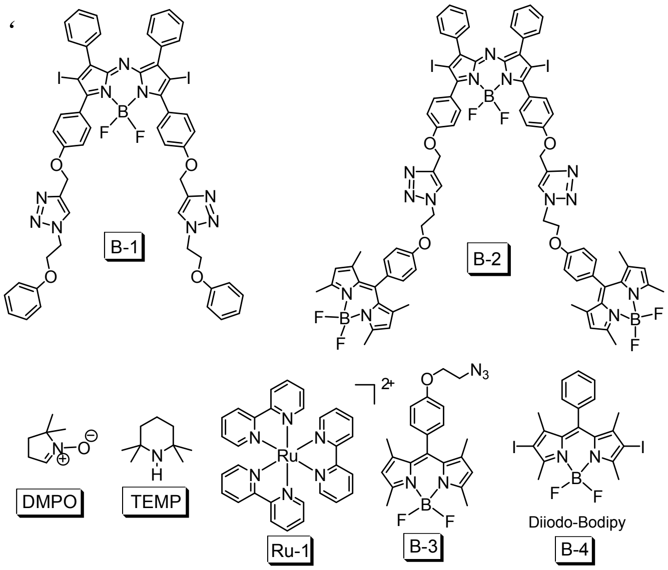
To a dried flask were added **B-1** or **B-2** (1 mol%), tetrahydroisoquinoline derivatives (0.1 mmol), acetylene derivatives (5 eq). The reaction mixture was stirred at room temperature (rt) under air atmosphere. The solution was then irradiated using a 35 W xenon lamp through a cut off filter (0.72 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 completion of the reaction, the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, DCM).

Results and Discussions

Design rationales of the organic photocatalysts

Aza-Bodipy show much red-shifted absorption than the normal Bodipy.[29-32] Iodo-aza-Bodipys have been used as triplet photosensitizers for produce of singlet oxygen ($^1O_2$).[31,33,34] However, this chromophore has not been used as triplet photosensitizer for photoredox catalytic organic reactions to prepare highly functionalized organic compounds. On the other hand, Bodipy-aza-Bodipy dyads have been reported for the FRET study.[35,36] However, without the iodination thus the heavy atom effect, the produce of triplet excited state is non-efficient, as a result, these FRET dyads cannot be used as photocatalysts for photocatalytic organic reactions.

Inspired by these studies, we used iodo-aza-Bodipy as photocatalyst for preparation of highly functionalized organic compounds. Furthermore, we constructed Bodipy-aza-Bodipy triad, in which RET was established, and the singlet energy acceptor aza-Bodipy was iodinated, therefore, the visible light-harvesting ability of the photocatalyst was enhanced with the RET effect. Bodipy-aza Bodipy triad was reported previously, but without iodination, it is unsuitable to be used as triplet photosensitizer.[36]



Scheme 1. Molecular structures of the photocatalysts **B-1** and **B-2**. The reference compounds **B-3**, **B-4**, **Ru-1** (Ru(bpy)$_3$Cl$_2$) , 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO, scavengers for $O_2^{\bullet-}$) and 2,2,6,6-tetramethylpiperidine (TEMP, scavengers for $^1O_2$) were also presented.

The synthesis of the organic photocatalysts are based on the routine chemistry of Bodipy and the aza-Bodipy (Scheme 1).[27] Cu(I)–promoted Click reaction was used to connect the two chromophores together. The products were obtained with satisfactory yields.

UV–vis absorption spectra of the photocatalysts

The UV-vis absorption of the compounds were studied (Fig. 1). Bodipy **B-3** gives absorption at 504 nm (ε = 82000 M^{-1} cm^{-1}). Conversely, aza-Bodipy **B-1** gives strong absorption at much red-shifted wavelength of 683 nm (ε = 73000 M^{-1} cm^{-1}). For the triad **B-2**, two absorption bands at 504 nm (ε = 165000 M^{-1} cm^{-1}) and 683 nm (ε = 71000 M^{-1} cm^{-1}) were observed, which can be attributed to the Bodipy and the iodo-aza-Bodipy units, respectively. The absorption spectrum of **B-2** is almost superimposable to the sum of Bodipy **(B-3)** and azaBodipy **(B-1)**, therefore these is no electronic interaction between the components in **B-2** at the ground state.[36,37] Compared to **B-2**, **B-4** only show one absorption band at 537 nm.

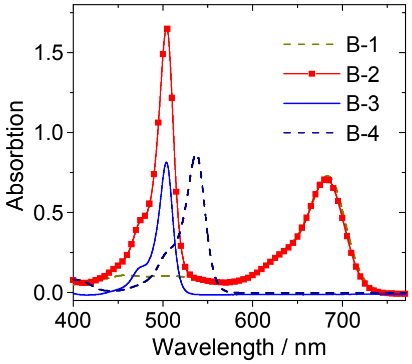


Fig. 1 UV-vis absorption spectra of **B-1**, **B-2** and **B-3**. c = 1.0×10^{-5} M in toluene. 20°C.

Table 1. Photophysical parameters of the organic triplet photosensitizers.

	λ_{abs} [a]	ε [b]	λ_{em}	Φ_F (%) [c]	τ_F / ns [d]	τ_T / μs [e]	Φ_Δ [l]
B-1	683	0.73	714	0.21 [f]	0.12 [i]	7.2 (4.8)	0.68 [g]
B-2	504 /683	1.65 /0.71	520 /714	0.53 [g]/0.15 [f]	0.06 [h] / 2.23 [i]	5.5 (3.7)	0.69 [g]
B-3	504	0.82	520	64.2	4.20	– [k]	– [k]
B-4	537	0.87	556	3.6	0.13	104.8	0.87
Ru-1 [m]	451	0.167	607	6.1	-	0.45	0.57

[a] In toluene (1.0×10^{-5} M). In nm. [b] Molar extinction coefficient. 10^5 M^{-1} cm^{-1}. [c] Fluorescence quantum yields. In CH_2Cl_2. [d] Fluorescence lifetimes in toluene. [e] Triplet state lifetimes, measured by transient absorption. In toluene. The values in parenthesis are measured in CH_3CN. [f] λ_{ex} = 660 nm. λ_{em} = 683 nm. [g] λ_{ex} = 480 nm, λ_{em} = 504 nm. [h] λ_{ex} = 470 nm, λ_{em} = 504 nm. [i] λ_{ex} = 670 nm, λ_{em} = 683 nm. [j] with methylene blue (MB) as standard (Φ_Δ□= 0.57), λ_{ex} = 675 nm. [k] Not applicable. [l] Quantum yield of singlet oxygen ($^1O_2$). [m] In acetonitrile (1.0×10^{-5} M). In nm. 20 °C.

The fluorescence emission of the compounds were investigated to study the intramolecular energy transfer for **B-2** (see ESI † Fig. S52).[27] Bodipy gives intense fluorescence at 520 nm (Φ_F = 64.2%). However, this emission band was quenched in **B-2**, indicates that energy transfer from the Bodipy part to the iodo-aza Bodipy part is significant in **B-2**.[27,35,36] However, the intramolecular electron transfer is a thermodynamically allowed process (See later section for detail). The triplet excited state lifetime of **B-2** (5.5 μs) is only slightly reduced compared with that of **B-1** (7.2 μs). Therefore we propose that the electron transfer is not significant for **B-2**. Notably **B-2** shows broadband absorption in the region of 400 nm – 750 nm. The triplet excited state lifetimes of **B-1** and **B-2** are longer than the conventional photocatalyst $Ru(bpy)_3Cl_2$. All these properties are beneficial for photoredox catalytic organic reactions.

Electrochemical properties

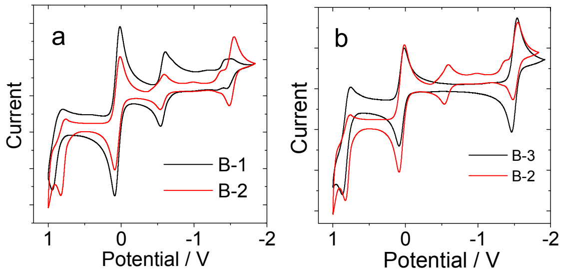


Fig. 2 Cyclic voltammogram of the dyad photosensitizer **B-1, B-2** and **B-3**. Ferrocene (Fc) was used as internal reference ($E_{1/2}$ = +0.40 V (Fc^+/Fc) vs. SCE). (a) **B-1** and **B-2**, (b) **B-2** and **B-3**. c = 1.0×10^{-3} M .In deaerated CH_3CN solutions containing 1.0 mM photosensitizers alone, or with the ferrocene, 0.10 M Bu_4NPF_6 as supporting electrolyte, Ag/$AgNO_3$ reference electrode, Scan rates: **B-1** and **B-3:** 0.1 V/s, **B-2:** 0.05 V/s. 20 °C.

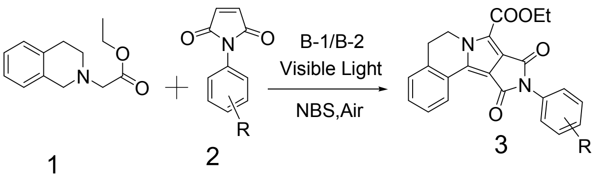
Table 2 Redox potentials of acceptors and the of free-energy changes (ΔG_{ET}, PET) for the potential intramolecular electron transfer (with Bodipy unit as electron donor and the iodo-aza BODIPY unit as electron acceptor in **B-2**). Anodic and cathodic peak potential were presented. The potential values of the compounds are vs. standard hydrogen electrode (with Fc as internal reference, for which $E_{1/2}$ (Fc^+/Fc) = +0.38 V vs. SCE (saturated calomel electrode).[a]

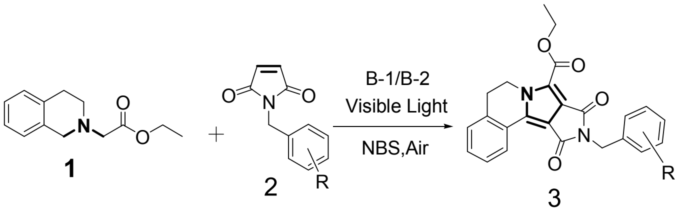
	E_{OX} (V)	E_{Red} (V)	ΔG_{ET} (eV)
B-1	– [b]	–0.22	– [b]
B-2	+1.15	–0.22, –1.21	–0.15 [c]
B-3	+1.15	–1.15	– [b]
1	+1.00	– [b]	– [b]

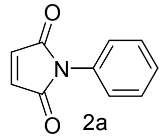
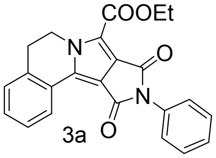
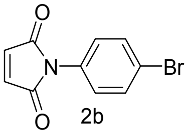
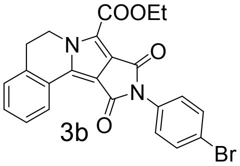
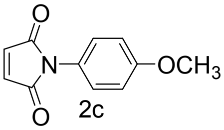
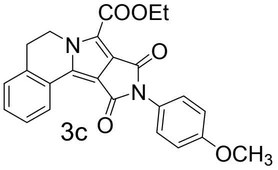
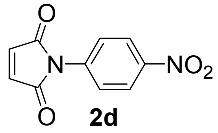
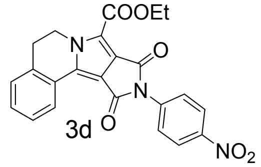
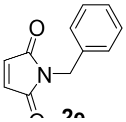
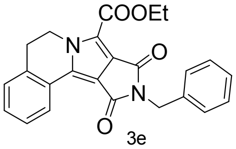
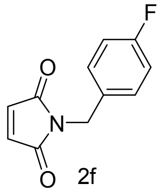
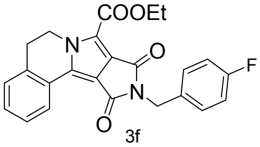
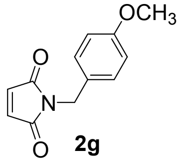
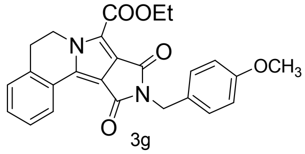
[a] Cyclic voltammetry in Ar saturated acetonitrile containing a 0.10 M Bu_4NPF_6 supporting electrolyte; Counter electrode is Pt electrode; working electrode is glassy carbon electrode; Ag/$AgNO_3$ couple as the reference electrode. c [Ag^+] = 0.1 M. 1.0 mM dyad photosensitizers in DCM, 20 °C. Conditions:1.0 mM dyad photosensitizers and 1.0 mM ferrocene in DCM, 20 °C. Calculated relative to SCE (saturated calomel electrode). [b] No reduction potential were observed, or no ΔGcs values were calculated. [c] The value of ΔGcs, with **B-3** unit as electron donor.

To study electrochemical properties of **B-1**, **B-2** and **B-3**, cyclic voltammetry of the compounds were measured (Fig. 2). For **B-1**, a reversible reduction at $E_{1/2}$ = –0.24V was observed. For **B-3**, a reversible reduction at $E_{1/2}$ = –1.17V and a reversible oxidation at $E_{1/2}$ = +1.13V was observed. **B-2** shows a reversible reduction at $E_{1/2}$= – 0.24V and an irreversible

Table 3. Oxidation/ [3+2] cycloaddition/ aromatization reactions.^{a}





Entry		Substrate	Product	t[h][b] (B-1/B-2)	Yield [c] (B-1/B-2)	TON	TOF/min^{-1}
1	1a	 2a	 3a	1.5/1.5	76/86	76/86	0.84/0.96
2	1a	 2b	 3b	1/1	71/82	71/86	1.18/1.43
3	1a	 2c	 3c	1.5/1.5	64/70	64/70	0.71/0.78
4	1a	 **2d**	 3d	1.5/1.5	72/80	75/80	0.83/0.89
5	1b		 3e	1.5/1.5	73/84	73/84	0.81/0.93
6	1b	 2f	 3f	1.5/1.5	77/83	77/83	0.86/0.92
7	1b	 **2g**	 3g	1.5/1.5	70/78	70/78	0.78/0.87

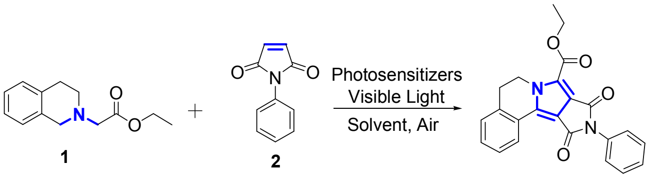
^{a} Reaction conditions: **1a** or **1b** (0.15 mmol), **2a** or **2b** (0.10 mmol), **B-1** or **B-2** (1mol%) and NBS (1.2 equiv) were mixed in dichloromethane (5.0 mL), the mixture was irradiated with 35 W Xe lamp (λ > 385 nm), R.T. ^{b} Reaction time with photosensitizers. ^{c} Yield of isolated products catalyzed with **B-1** and **B-2.**

oxidation at $E_{1/2}$= +1.13V, which are similar to that of the sum of **B-1** and **B-3**. This result indicates that there is no electronic exchange between bodipy part and azabodipy part of triad **B-2** at ground state. With approximation of the T_1 state energy level of iodo-aza-Bodipy as 1.2 eV, The free energy changes ($\Delta G°$) of the photoinduced intramolecular electron transfer in **B-2** was determined as +0.15 eV according to Rehm-Weller equation, with Azabodipy as electron acceptor, and the postulation that the electron transfer occurs via the triplet state of the azaBodipy part, since our previous study shows that the FRET is a ultrafast process.[27] This result indicates that electron transfer from Bodipy unit to iodo-Aza Bodipy unit is unlikely.

The intermolecular electron transfer between the photocatalyst and the substrate was studied. Firstly, the electrochemical properties of compound **1** was studied. **1** shows a irreversible oxidation at $E_{1/2}$ = +1.00V. The free energy changes for the electron transfer from compound **1** to the triplet excited state of **B-2** was determined as −0.04 eV. For all the details about the electrochemical studies (ESI†, section 11).

Oxidation/[3+2] cycloaddition/oxidative aromatization with tetrahydroisoquinoline to construct pyrrolo[2,1-a]isoquinolines

Table 2 Optimization of the reaction conditions [a]



	Time / h	Solvents	Power / W/m^2	Yield / %[b]
B-2	1.0	CH_3CN	300	53.6
B-2	1.0	CH_2Cl_2	300	75.1
B-2	1.5	CH_2Cl_2	300	85.5
B-1	1.0	CH_2Cl_2	300	67.4
B-1	1.5	CH_2Cl_2	300	76.4
None	2.0	CH_2Cl_2	300	trace
B-2	2.0	CH_2Cl_2	0	trace
B-4	1.5	CH_2Cl_2	300	79.2
Ru(bpy)$_3$Cl$_2$	3.0	CH_2Cl_2	300	33.6

[a] Reaction conditions: **1** (0.15 mmol), **2** (0.10 mmol), **B-1**, **B-2** or **B-4** (1mol%) , air, 35W Xenon light irradiation (λ > 385 nm), NBS (1.2 equiv), and solvent (5.0 mL), rt. [b] Yield of the isolated product.

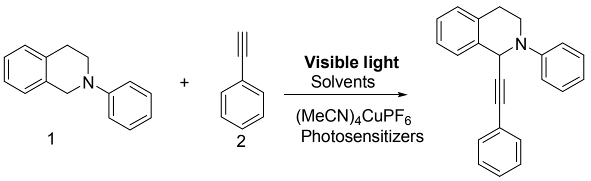
Recently a [3+2] cycloaddition/aromatization tandem reaction was studied with Ru(bpy)$_3$Cl$_2$ as the photocatalysts.[11] The product pyrrolo[2,1-*a*]isoquinolines are the important building blocks of bioactive natural products. This reaction is particularly interesting because highly functionalized organic compounds can be prepared under mild condition and a concise synthetic approach. Therefore we consider this reaction as a ideal exemplar to screen new organic photocatalysts. With Ru(bpy)$_3$Cl$_2$ as the photocatalyst, the reaction times were long (11 h–25 h).[11] Recently we reported iodo-Bodipy as photocatalysts for this reaction.[38-40] However, those photocatalysts are based on the conventional mono-chromophore profile, and the photocatalyst show only one major absorption band in the visible spectral region. Therefore, much room is left to improve the visible light-harvesting efficiency of these mono-chromophore based photocatalysts, especially in the case of a *panchromatic* light source was used for the photoredox catalytic organic reactions, such as white light from xenon lamp, or halogen lamp, or solar light.[26,27]

We studied this [3+2] cyclic addition reaction between tetrahydroisoquiniline and maleimide derivatives with **B-1**, **B-2** and **B-4** as the photocatalysts. The reactions proceed smoothly with dichloromethane as the solvent, the reaction time was reduced to 1 – 1.5 h, with satisfactory yield of 64% – 86 % (Table 3). Previously **B-4** was reported as an efficient photocatalyst for [3+2] cyclic addition reaction.[40] We found that the yield with **B-2** as photocatalyst is higher than that with **B-1** and **B-4** under the same experimental conditions. Moreover, we found that the reaction can be carried out with solar light as the excitation source (See ESI †, section 7).

Next, the substrates tolerance of the [3+2] cycloaddition/aromatization tandem reaction were studied (entry 1-4, Table 3). The *N*-aryl succinimide substrates with electron-neutral, withdrawal and electron-donating substituents were studied. All substrates give good yields. In all the cases high yields were observed with **B-2** than that with **B-1** as the photocatalyst. This improved photocatalytic efficiency can be attributed to the higher visible light-harvesting ability of **B-2** (Fig. 1).

Coupled photocatalytic aerobic oxidation and Cu(I) catalyzed alkynylation reactions : C–C bond formation

Table 4 Optimization of the reaction conditions of the coupled photocatalytic oxidation and the Cu(I) Catalyzed Alkynylation Reactions [a]

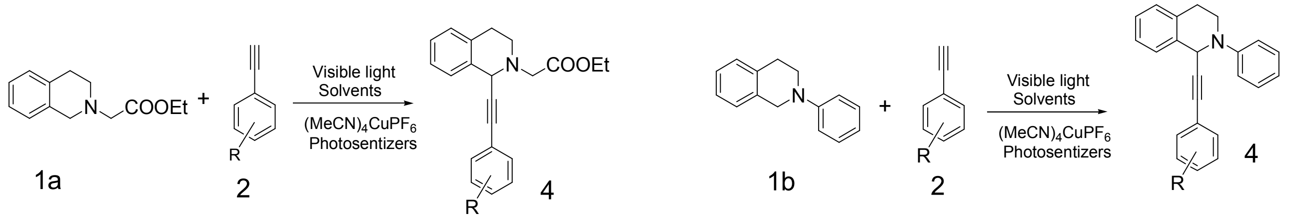


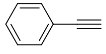
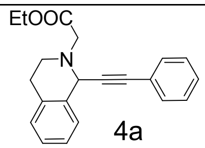
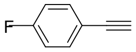
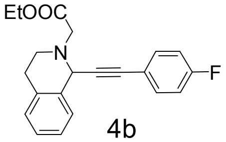
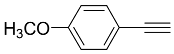
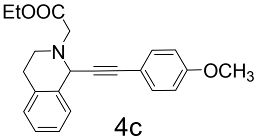
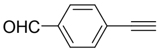
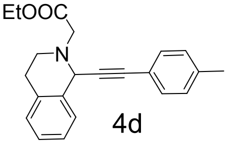
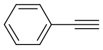
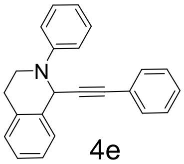
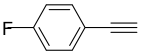
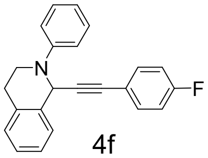
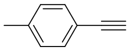
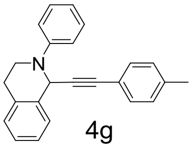
Entry	Catalysis	Time / h	Solvents	Power / W/m^2	Yield / %[b]
1	**B-1**	3.0	CH_2Cl_2	300	27.4
2	**B-1**	3.0	EtOAc	300	15
3	**B-1**	2.0	CH_3CN	300	71
4	**B-1**[c]	3.0	CH_3CN	300	0
5	**B-1**	3.0	CH_3CN	0	trace
6	**B-2**	2.0	CH_3CN	300	80
7	**None**	3.0	CH_3CN	300	8
8	**Ru(bpy)$_3$Cl$_2$**	3.0	CH_3CN	300	43

[a] Reaction conditions: **1** (0.10 mmol), **2** (0.8 mmol), photocatalyst catalysis **B-1** or **B-2** (1mol%) , air, 35 W Xe light irradiation (λ > 385 nm), (MeCN)$_4$CuPF$_6$ (10 mol%), and solvent (2.0 mL), rt. [b] Yield of the isolated product. [c] Without (MeCN)$_4$CuPF$_6$.

Coupled photocatalytic and metal catalyzed reaction is a fascinating research area. In this case the photocatalytic cycle and the metal catalytic cycle must be concertedly coupled,

Table 5. Scope of the photooxidation–alkynylation reaction catalyzed by **B-1** and **B-2**[a]



Entry		Substrate	Product	t [h][b] (**B-1**/**B-2**)	Yield[c] (**B-1**/**B-2**)	TON[d]	TOF/ min^{-1e}
1	1a	 2a	 4a	2/2	59/61	59/61	0.49/0.51
2	1a	 2b	 4b	3/3	49/53[f]	49/53	0.27/0.29
3	1a	 2c	 4c	4/4	52/55[f]	52/55	0.22/0.23
4	1a	 2d	 4d	4/4	53/57[f]	53/57	0.22/0.24
5	1b	 2a	 4e	2/2	71/80	71/80	0.59/0.67
6[g]	1b	 2b	 4f	4/4	67 / 73	67/73	0.28/0.30
7	1b	 2c	 4g	4/4	61/71[f]	61/71	0.25/0.30

[a] Reaction conditions: **1a** or **1b** (0.10 mmol), **4a-g** (0.50 mmol), **B-1** and **B-2** (1mol%) and (MeCN)$_4$CuPF$_6$ (0.01 mmol) were mixed in CH$_3$CN (3.0 mL), the mixture was irradiated with 35 W Xe lamp (λ > 385 nm), 20 °C. [b] Reaction time with photosensitizers. [c] Yield of isolated products catalyzed with **B-1** and **B-2**. [d] Turnover number. [e] Turnover frequency. [f] In dichloromethane. [g] CuI (0.01 mmol).

otherwise the reaction won't be successful. Recently a coupled photocatalytic aerobic oxidation and the Cu(I) catalyzed was reported.[28] The photocatalyst is the conventional complex Ru(bpy)$_3$[PF$_6$]$_2$, which shows weak absorption in visible spectral region. As a result, the reaction times were long (16–36 h).[28] In order to study the photocatalytic property of the organic triplet photosensitizers such as iodo-aza-Bodipy photocatalysts, **B-1** and **B-2** were used as photocatalyst for the coupled photocatalytic oxidation and the Cu(I)-catalyzed alkynylation of tetrahydroisoquinoline (Table 4).

We found that both **B-1** and **B-2** can promote the coupled dual-catalytic reaction smoothly. The reaction time was reduced to 2–4 h. Previously with the conventional photocatalyst Ru(bpy)$_3$[PF$_6$]$_2$, the reaction times were in the range of 16–36 h.[28] Our results show that under the same alkynylation reaction with tetrahydroisoquinoline as substrates experimental conditions, $Ru(bpy)_3Cl_2$ gives much lower yields than that with **B-1** and **B-2** as the photocatalysts (Table 4). We also carried out control experiments in the absence of either the photocatalyst (**B-1** or **B-2**) or the metal complex $(MeCN)_4CuPF_6$ (entry 4 and 7 in Table 4). The results indicated that both catalysts are mandatory for the coupled catalytic reactions.

The scope of both the tetrahydroisoquinoline and the phenylalkyns were extended (Table 5). Phenyl alkynes with electron neutral, withdrawal and donating substituents give satisfactory yields. Different substitutions on N atom of tetrahydroisoquinoline do not hamper the coupled photocatalytic/Cu(I) catalytic reaction.

Mechanism Studies

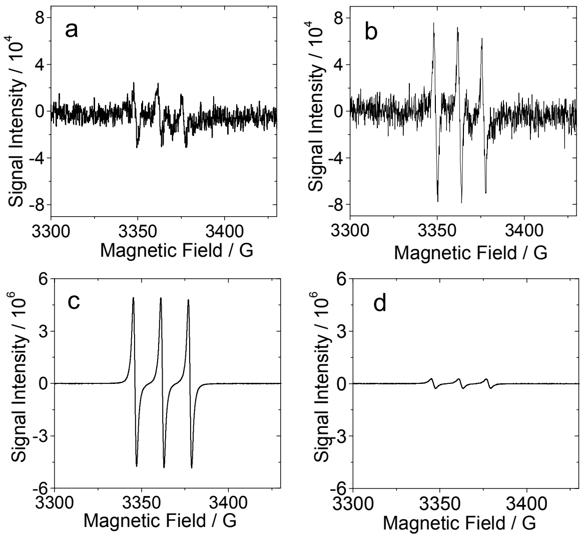
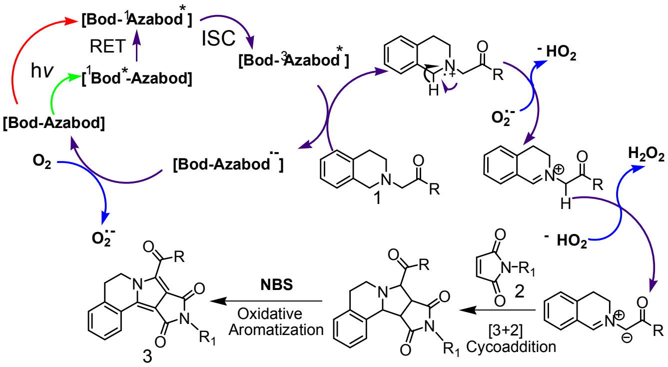


Fig. 3 (a) ESR spectrum of the mixture **B-2** (4.0×10^{-4} M) and DMPO (2.0×10^{-2} M); (b) ESR spectrum of the mixture **B-2** (4.0×10^{-4} M), **1a** (5.0×10^{-2} M) and DMPO (2.0×10^{-2}M); (c) **B-2** (4.0×10^{-4} M), TEMP (0.10M); (d) **B-2** (4.0×10^{-4} M), TEMP (0.10 M), **1a** (5.0×10^{-2} M). In air saturated CH_3CN. All the irradiations were performed with 635 nm continuous laser and the duration is 120 s (210 mW/cm^2). 22 °C.

The mechanism of the photocatalytic reactions were studied with the electron spin resonance (ESR) spectroscopy. For the [3+2] cycloaddition/aromatization tandem reaction, it was proposed that singlet electron transfer (SET) from the tetrahydroisoquinoline to the photoexcited state of the photocatalysts is responsible for the initialization of the photocatalytic cycles. Observation of the superoxide anion radical ($O_2^{\bullet-}$) supports the putative mechanism.[11,38-40] With the new photocatalysts **B-1** and **B-2**, however, it is necessary to confirm the photocatalytic mechanism. The reaction mechanism was studied with electron spin resonance (ESR) spectroscopy (Fig. 3). 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) and 2,2,6,6-tetramethylpiperidine (TEMP) were used as scavengers for $O_2^{\bullet-}$ and $^1O_2$, respectively.[15, 40] With DMPO, ESR signal attributed to its adduct with $O_2^{\bullet-}$ was detected for the mixture of **B-1** and substrate **1** upon photoirradiation (Fig. 3b), but the signal was much weaker in the absence of amine substrate 1a, indicating that electron transfer from the substrate to **B-1** is crucial for formation of $O_2^{\bullet-}$. The experiment with TEMP shows that $^1O_2$ was produced with **B-1** in the absence of substrate (1a) (Fig. 3c). With addition of the substrate **1a**, no ESR signal due to $^1O_2$ was detected, indicate that produce of $^1O_2$ is completely inhibited by electron transfer from substrate **1a** to **B-1** (Fig. 3d). Therefore the electron transfer from the amine substrate to the organic triplet photosensitizer is confirmed.

Scheme 2. Proposed [3+2] cycloaddition/ aromatization tandem reaction mechanism.



The proposed mechanism is presented in Scheme 2. With Bodipy-iodo Aza Bodipy triad (**B-2**) was photoirradiated with the white light (broadband) of xenon lamp, Bodipy singlet excited state (^{1}Bod*) and iodo AzaBodipy singlet excited state (^{1}AzaBod*) are produced. ^{1}Bod* is able to transfer the energy to AzaBod by RET process. Then ^{3}AzaBod* is populated by ISC. Electron transfer from tetrahydroisoquinoline substrate to ^{3}AzaBod* to produce Azabod anion and high active iminium species of the tetrahydroisoquinoline. Azabod anion returns to ground state through transferring electron to O_2 then $O_2^{\bullet-}$ is produced. $O_2^{\bullet-}$ can capture two proton from tetrahydroisoquinoline substrate cation to form zwitterion and H_2O_2, which is also supported by ^{1}H NMR (see ESI†, Fig. S56). Zwitterion species react with maleic anhydride derivatives then oxidized by NBS to obtain target molecules.

The mechanism of dual catalysis also was studied with ESR and NMR. We proposed that the electron transfer from the tetrahydroisoquinoline substrate to the organic triplet photosensitizer then Cu(I) catalyze the coupled reaction between iminium species of the tetrahydroisoquinoline and phenylalkyns derivatives (for the detailed measurement result, please refer to ESI †, Scheme S1).

Conclusions

In summary, Bodipy-iodo AzaBodipy triad and iodo-aza Bodipy triplet photosensitizers were used as photocatalysts for photoredox catalytic organic reactions. Different from the conventional photocatalysts such as $Ru(bpy)_3Cl_2$, Eosin Y or

Rose Bengal, which contain only a single visible light-harvesting unit, the new photocatalysts show strong absorption in visible spectral region. Furthermore, the triad shows strong *broadband* absorption in 400 nm – 750 nm range. Both compounds show high singlet oxygen quantum yields, indicating efficient ISC. These compounds were used as novel photocatalysts for two photoredox catalytic organic reactions with tetrahydroisoquinilines as substrates to prepare highly functionalized organic compounds via the [3+2] cycloaddition/aromatization tandem reaction, as well as the Cu(I) catalyzed alkynylation reactions. We found that triad photocatalyst with broadband visible light absorption is more efficient than the monochromophore photocatalyst (2,6-diiodo-aza-Bodipy). Furthermore, the iodo-Aza Bodipy is more efficient than the conventional photocatalysts such as $[Ru(bpy)_3]Cl_2$. Our results are useful for designing of efficient organic triplet photosensitizers as photocatalysts to improve the photoredox catalytic organic reactions.

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Notes and references

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† Electronic Supplementary Information (ESI) available: molecular structure characterization data, emission spectra, CV data and all the detailed information we mentioned in text. See DOI: 10.1039/b000000x/

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