RSC Advances

PAPER



Cite this: RSC Adv., 2014, 4, 36131

Received 21st April 2014 Accepted 25th July 2014 DOI: 10.1039/c4ra03631j

www.rsc.org/advances

1. Introduction

Photoredox catalytic organic reactions have attracted a great deal of attention.¹⁻⁸ Using this novel synthetic method, highly functionalized organic compounds can be prepared in good yield and selectivity under mild reaction conditions. It has been demonstrated that a wide variety of reactions can be improved using the photocatalytic approach, including those involving the generation of radicals, particularly dehalogenation, dehydrogenation coupling and [3 + 2] cycloadditions.¹⁻⁶ However, the photocatalysts used for these organic reactions are restricted to off-the-shelf compounds such as Ru(bpy)₃Cl₂,^{2,9-14} and a few xanthene dyes such as Eosin Y and Rose Bengal.15-20 These conventional photocatalysts have disadvantages, for example Ru(bpy)₃Cl₂ gives weak absorption in the visible region.²¹ In the case of Eosin Y and Rose Bengal it is difficult to modify the molecular structure, and as a result the redox potentials of the photocatalysts cannot be readily adapted for different substrates.

On the other hand organic compounds have readily derivatizable molecular structures, but organic triplet



Song Guo, Renjie Tao and Jianzhang Zhao*

The 4-bora-3*a*,4*a*-diaza-*s*-indacene scaffold is known as Bodipy. 2,6-Diiodo-aza-Bodipy (**B-1**) and the Bodipy-2,6-diiodo-aza-Bodipy triad (**B-2**) have been used as novel photocatalysts for photoredox catalytic organic reactions with tetrahydroisoquiniline as substrate to prepare highly functionalized organic compounds *via* a [3 + 2] cycloaddition–aromatization tandem reaction and Cu(i)-catalyzed alkynylation reactions. In distinction to conventional photocatalysts such as Ru(bpy)₃Cl₂, Eosin Y or Rose Bengal, which are based on a mono-visible light-harvesting chromophore profile and show weak absorption in the visible region, the new photocatalysts are strong visible absorbers (**B-1**, ε = 73 000 M⁻¹ cm⁻¹ at 683 nm). More importantly, resonance energy transfer (RET) has been used to increase the absorption of photocatalysts **B-2** in the visible region, in which two Bodipy units were used as energy donor and diiodo-aza-Bodipy as energy acceptor. **B-2** shows broadband absorption in the range 400–750 nm (ε = 165 000 M⁻¹ cm⁻¹ at 504 nm, and 71 000 M⁻¹ cm⁻¹ at 683 nm). Iodo-aza-Bodipy is more efficient than conventional photocatalysts such as [Ru(bpy)₃]Cl₂. Furthermore, the broadband visible light-absorbing **B-2** is more efficient as a photocatalyst than previously reported monochromophore photocatalyst **B-4** (diiodo-Bodipy). Our results will be useful for the design of efficient organic triplet photosensitizers as photocatalysts for photoredox catalytic organic reactions.

photosensitizers are rarely reported, since the intersystem crossing (ISC) is often very weak in neat organic chromophores.^{22,23} Furthermore, all conventional photocatalysts share a similar feature, which is that the molecule contains only a single light-absorbing unit.²³ The excitation energy of a broadband light source (*e.g.* white light, including solar light) cannot therefore be efficiently harvested by these photocatalysts. These features may diminish their catalytic efficiency, and it is therefore highly desirable to design new organic photocatalysts to overcome these issues.

Before discussing the design of triplet photosensitizers as new photocatalysts, it is useful to have a brief outline of the mechanisms of photoredox catalytic organic reactions. Single electron transfer (SET) between photocatalyst and substrate is the most popular mechanism for photoredox catalytic reactions.^{1,5,24} Owing to the bimolecular character of the SET, certain properties of a photocatalyst are crucial:²⁵ (a) light-absorbing ability, (b) the lifetime of the triplet excited states, and (c) ease of modifying the molecular structure, in order that the redox potential of the photocatalyst can easily be tuned to achieve selectivity or to improve its catalytic efficiency. It is very difficult, if not impossible, however, to address these challenges with conventional photocatalysts such as Ru(bpy)₃Cl₂, Eosin Y or Rose Bengal.^{1,23}

For this reason we chose iodo-aza-Bodipy as the basis of new photocatalysts. Importantly, we devised resonance energy

YAL SOCIETY CHEMISTRY

View Article Online

View Journal | View Issue

State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China. E-mail: zhaojzh@dlut.edu.cn; Fax: +86 411-8498-6236

[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/c4ra03631j

transfer (RET) triplet photosensitizers, which are based on two different chromophores and show broadband absorption in the visible region to improve light absorption.^{26,27} We found that organic photocatalysts were efficient in two different bench mark reactions, the tetrahydroisoquinoline-based [3 + 2] cycloaddition–aromatization tandem reaction,^{6,11} and the coupled Cu(1)-catalyzed alkynylation of tetrahydro-isoquinolines.²⁸ We demonstrated that dyad photocatalysts with the RET effect are more efficient than mono-chromophore-based photocatalysts. Furthermore, even the mono-chromophore iodo-aza-Bodipy photocatalyst possessed greater photocatalytic efficacy than conventional photocatalysts such as Ru(bpy)₃Cl₂. Our results will be helpful in the design of new organic photocatalysts to improve photoredox-catalysed organic reactions.

2. Experimental

2.1 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; a superoxide radical anion O_2 ^{•–} scavenger), or 2,2,6,6-tetramethylpiperidine (TEMP; a singlet oxygen ${}^{1}O_2$ scavenger) in aerated CH₃CN were stirred together in the dark and the solution then injected into quartz capillaries. A diode-pumped solid state (DPSS) continuous laser (635 nm) was used for photoirradiation of the solution in the quartz capillaries for 120 s.

2.2 General procedure for the oxidation and [3 + 2] cycloaddition–aromatization tandem reaction with tetrahydroisoquinoline derivatives catalyzed by organic triplet photosensitizers B-1 and B-2

1 (0.15 mmol), photosensitizers (1 mmol%) and 2 (0.1 mmol) were dissolved in dichloromethane (DCM; 5 mL). 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 to light >385 nm). Thin-layer chromatography (TLC) was used to monitor the progress of the reaction. *N*-Bromosuccinimide (NBS; 25 mg) was added to the reactor. After 5 min the solvents were removed and the residue purified by column chromatography (silica gel, DCM).

2.3 General procedure for 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), and acetylene derivatives (5 equiv.). The reaction mixture was stirred at room temperature in air. 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 to light >385 nm). TLC was used to monitor the progress of the reaction. After the reaction was complete, the solvent was evaporated under reduced pressure and the residue purified by column chromatography (silica gel, DCM).

3. Results and discussion

3.1 Design rationale of the organic photocatalysts

Aza-Bodipy shows much greater red-shifted absorption than normal Bodipy.²⁹⁻³² Iodo-aza-Bodipys have been used as triplet



Scheme 1 Molecular structures of the photocatalysts B-1 and B-2. The reference compounds B-3, B-4, Ru-1 (Ru(bpy)₃Cl₂), 5,5-dimethyl-1-pyrroline-N-oxide (DMPO; scavenger for O₂⁻) and 2,2,6,6-tetramethylpiperidine (TEMP; scavenger for ¹O₂) are also illustrated.

Paper

photosensitizers for producing singlet oxygen $({}^{1}O_{2}).^{31,33,34}$ However, this chromophore has not been used as a triplet photosensitizer for photoredox-catalysed organic reactions to prepare highly functionalized organic compounds. On the other hand, Bodipy-aza-Bodipy dyads have been reported for fluorescence resonance energy transfer (FRET) study.^{35,36} However, in the absence of the heavy atom effect resulting from iodination, the production of a triplet excited state is ineffective, and as a result these FRET dyads cannot be used as photocatalysts in organic reactions.

Inspired by previous studies, we selected iodo-aza-Bodipy as photocatalyst for the preparation of highly functionalized organic compounds. In addition we constructed the Bodipy-aza-Bodipy triad, in which RET was established, and the singlet energy acceptor aza-Bodipy was iodinated. The visible lightharvesting ability of the photocatalyst was thus enhanced by the RET effect. The Bodipy-aza-Bodipy triad has been reported previously, but without iodination it is unsuitable for use as a triplet photosensitizer.³⁶

The synthesis of the organic photocatalysts is based on the routine chemistry of Bodipy and aza-Bodipy (Scheme 1).²⁷ The Cu(i)-promoted click reaction was used to connect the two chromophores together. The products were obtained in satisfactory yield.

3.2 UV-Vis absorption spectra of the photocatalysts

The UV-Vis absorption of the compounds was determined (Fig. 1). Bodipy **B-3** gave absorption at 504 nm ($\varepsilon = 82\ 000\ \text{M}^{-1}\ \text{cm}^{-1}$).



Fig. 1 UV-Vis absorption spectra of B-1, B-2 and B-3. $c = 1.0 \times 10^{-5}$ M in toluene; 20 °C.

Table 1	Photophysical	parameters	of the organic	triplet	photosensitizers
---------	---------------	------------	----------------	---------	------------------



Fig. 2 Cyclic voltammograms of the dyad photosensitizers (a) **B-1** and **B-2**, and (b) **B-2** and **B-3**. Scan rates: **B-1** and **B-3**: $0.1 \vee s^{-1}$, **B-2**: $0.05 \vee s^{-1} 20 \circ C$. Ferrocene (Fc) was used as internal reference ($E_{1/2} = +0.40 \vee (Fc^+/Fc) \vee s$. SCE). $c = 1.0 \times 10^{-3} M$. Measurements were made in deaerated CH₃CN solution containing 1.0 mM photosensitizers alone, or with the ferrocene, 0.10 M Bu₄NPF₆ as supporting electrolyte; Ag/AqNO₃ reference electrode.

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) = +0.4 V vs. SCE (saturated calomel electrode)^{*a*}

	$E_{\mathrm{Ox}}\left(\mathrm{V}\right)$	$E_{\rm Red}$ (V)	$\Delta G_{\mathrm{ET}} (\mathrm{eV})$
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
в-2 В-3 1	+1.15 +1.15 +1.00	-0.22, -1.21 -1.15 -b	-0.15° $-^{b}$ $-^{b}$

^{*a*} Cyclic voltammetry in Ar saturated acetonitrile containing a 0.10 M Bu₄NPF₆ supporting electrolyte; counter electrode is Pt electrode; working electrode is glassy carbon electrode; Ag/AgNO₃ couple as the reference electrode. *c* [Ag+] = 0.1 M. 1.0 mM dyad photosensitizers in CH₃CN, 20 °C. Conditions: 1.0 mM dyad photosensitizers and 1.0 mM ferrocene in CH₃CN, 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.

Conversely, aza-Bodipy **B-1** gave strong absorption at the greatly red-shifted wavelength of 683 nm ($\varepsilon = 73\ 000\ M^{-1}\ cm^{-1}$). For the triad **B-2**, two absorption bands at 504 nm ($\varepsilon = 165\ 000\ M^{-1}\ cm^{-1}$) and 683 nm ($\varepsilon = 71\ 000\ M^{-1}\ cm^{-1}$) were observed, which may be attributed to the Bodipy and the iodo-aza-Bodipy units, respectively. The absorption spectrum of **B-2** is almost superimposable

	$\lambda_{ m abs}{}^a$	ε^{b}	λ_{em}	$\Phi_{\mathrm{F}}^{}c}$ (%)	$\tau_{\rm F}^{~d}/{ m ns}$	$\tau_{\mathrm{T}}^{e}/\mu\mathrm{s}$	${\Phi_\Delta}^l$
B-1	683	0.73	714	0.21^f	0.12^i	7.2 (4.8)	0.68 ^j
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 ^j
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
$\mathbf{Ru-1}^{m}$	451	0.167	607	6.1	—	0.45	0.57

^{*a*} In toluene $(1.0 \times 10^{-5} \text{ M})$ (nm). ^{*b*} Molar extinction coefficient $(10^5 \text{ M}^{-1} \text{ cm}^{-1})$. ^{*c*} Fluorescence quantum yields (in CH₂Cl₂). ^{*d*} Fluorescence lifetimes (in toluene). ^{*e*} Triplet state lifetimes, measured by transient absorption (in toluene; values in parentheses are in CH₃CN). ^{*f*} $\lambda_{ex} = 660 \text{ nm}, \lambda_{em} = 683 \text{ nm}.$ ^{*g*} $\lambda_{ex} = 480 \text{ nm}, \lambda_{em} = 504 \text{ nm}.$ ^{*h*} $\lambda_{ex} = 470 \text{ nm}, \lambda_{em} = 504 \text{ nm}.$ ^{*i*} $\lambda_{ex} = 670 \text{ nm}, \lambda_{em} = 683 \text{ nm}.$ ^{*j*} With methylene blue (MB) as standard ($\Phi_{\Delta}\Delta = 0.57$), $\lambda_{ex} = 675 \text{ nm}.$ ^{*k*} Not applicable. ^{*i*} Quantum yield of singlet oxygen (¹O₂). ^{*m*} In acetonitrile ($1.0 \times 10^{-5} \text{ M}$) (in nm at 20 °C).

on the sum of Bodipy (**B-3**) and aza-Bodipy (**B-1**), and there is therefore no electronic interaction between the components of **B-2** in the ground state.^{36,37} Compared to **B-2**, **B-4** showed only a single absorption band at 537 nm.

A summary of the photophysical parameters of the organic triplet photosensitizers is given in Table 1.

The fluorescence emission of the compounds was investigated to study the intramolecular energy transfer for **B-2** (see ESI, Fig. S52†).²⁷ Bodipy gives intense fluorescence at 520 nm ($\Phi_{\rm F} = 64.2\%$). However, this emission band was quenched in **B-**2, indicating that energy transfer from the Bodipy component to the iodo-aza-Bodipy component was significant in **B-2**.^{27,35,36} However, the intramolecular electron transfer is a thermodynamically allowed process (discussed in detail later). The triplet excited state lifetime of **B-2** (5.5 µs) was only slightly reduced compared to that of **B-1** (7.2 µs). We therefore propose that electron transfer is not significant in **B-2**. Notably, **B-2** shows broadband absorption in the region 400–750 nm. The triplet excited state lifetimes of **B-1** and **B-2** are longer than those of the conventional photocatalyst Ru(bpy)₃Cl₂. All these properties are beneficial in photoredox catalytic organic reactions.

3.3 Electrochemical properties

To study the electrochemical properties of B-1, B-2 and B-3, the cyclic voltammetry of the compounds was measured (Fig. 2). In the case of **B-1** a reversible reduction at $E_{1/2} = -0.24$ V was observed, and for B-3 a reversible reduction at $E_{1/2} = -1.17$ V and a reversible oxidation at $E_{1/2} = \pm 1.13$ V were observed. B-2 showed a reversible reduction at $E_{1/2} = -0.24$ V and an irreversible oxidation at $E_{1/2} = +1.13$ V, which are similar to the sum of B-1 and B-3 (Table 2). This result indicates that there is no electron exchange between the Bodipy and aza-Bodipy components of the triad B-2 at the ground state. With approximation of the T_1 state energy level of iodo-aza-Bodipy as 1.2 eV, the free energy changes (ΔG°) of the photoinduced intramolecular electron transfer in B-2 was determined as +0.15 eV according to Rehm-Weller equation, with aza-Bodipy as electron acceptor. It is postulated that the electron transfer occurs via the triplet state of the aza-Bodipy part, since our previous study showed that the FRET is an ultrafast process.²⁷ This result indicates that electron transfer from the Bodipy to the 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 an irreversible oxidation at $E_{1/2} = +1.00$ V. 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. Details of the electrochemical studies are given in ESI, Section 11.†

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

Recently a [3 + 2] cycloaddition–aromatization tandem reaction has been studied, using Ru(bpy)₃Cl₂ as photocatalyst.¹¹ The products, pyrrolo[2,1-*a*]isoquinolines, are important building blocks for bioactive natural products. This reaction is particularly interesting, because it means that highly functionalized organic compounds can be prepared under mild conditions using a concise synthetic approach. We therefore consider this reaction ideal for screening new organic photocatalysts (Table 3).

With $\operatorname{Ru}(\operatorname{bpy})_3\operatorname{Cl}_2$ as photocatalyst, the reaction times were long (11–25 h).¹¹ Recently we reported the use of iodo-Bodipy as photocatalyst for this reaction.^{38–40} However, these photocatalysts are based on a conventional mono-chromophore profile, and they show only one major absorption band in the visible spectrum. There is therefore much room for improving the visible light-harvesting efficiency of these monochromophore-based photocatalysts, especially in cases where a panchromatic light source is used for the photoredox catalytic organic reactions, such as white light from a xenon or solar light (Table 4, and ESI, Section 7†).^{26,27}

We studied the [3 + 2] cyclic addition reaction between tetrahydroisoquiniline and maleimide derivatives with **B-1**, **B-2** or **B-4** as photocatalyst. The reactions proceeded smoothly with dichloromethane as solvent, and the reaction time was reduced to 1–1.5 h, with satisfactory yields in the range 64–86% (Table 4). **B-4** was previously reported as an efficient photocatalyst for [3 + 2] cyclic addition reactions.⁴⁰ We found that the yield with **B-2** as photocatalyst was higher than that with **B-1** and **B-4** under similar experimental conditions. Moreover, we found that the reaction could be carried out with solar light as excitation source (see ESI, Section 7†).

Next, the substrate tolerance of the [3 + 2] cycloadditionaromatization tandem reaction was studied (Table 4, entries 1– 4). *N*-Aryl succinimide substrates with electron-neutral, electron-withdrawing or electron-donating substituents were included. All the substrates gave good yields. In each case higher yields were observed using **B-2** rather than **B-1** as





	Time/h	Solvents	Power/W m ⁻²	Yield ^b /%
B-2	1.0	CH ₃ CN	300	53.6
B-2	1.0	CH ₂ Cl 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
$Ru(bpy)_3Cl_2$	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** (1 mol%), air, 35 W Xenon light irradiation ($\lambda > 385$ nm), NBS (1.2 equiv.), and solvent (5.0 mL), rt. ^{*b*} Yield of the isolated product.





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

3.5 Coupled photocatalytic aerobic oxidation and Cu(1)catalyzed alkynylation reactions: C-C bond formation

Coupled photocatalytic and metal-catalyzed reactions are a fascinating area of research. In this case the photocatalytic and metal catalytic cycle must be precisely coupled, otherwise the reaction will not be successful. Recently a photocatalytic aerobic oxidation coupled with Cu(1) catalysis was reported. The photocatalyst was a conventional complex, $Ru(bpy)_3[PF_6]_2$, which shows weak absorption in the visible region. As a result, the reaction times were long (16-36 h).²⁸ In order to study the photocatalytic properties of organic triplet photosensitizers such as iodo-aza-Bodipy photocatalysts, B-1 and B-2 were used as photocatalysts for the coupled photocatalytic oxidation and the Cu(I)-catalyzed alkynylation of tetrahydroisoquinoline (Table 5). We found that either B-1 or B-2 were able to promote the coupled dual-catalytic reaction smoothly, and the reaction time was reduced to 2-4 h. Previously, with the conventional photocatalyst Ru(bpy)₃[PF₆]₂, reaction times were as long as 16-36 h.28 Our results show that under similar experimental conditions, in alkynylation reaction with tetrahydroisoquinoline as substrates Ru(bpy)₃Cl₂ gives much lower yields than that B-1 and B-2 as photocatalysts (Table 5). We also carried out control experiments in the absence of either the photocatalyst (B-1 or B-2) or the metal complex (MeCN)₄CuPF₆ (entries 4 and 7 in Table 5). The results indicated that the two catalysts are suitable for coupled catalytic reactions.

Table 5Optimization of the reaction conditions of the coupledphotocatalytic 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 ₂ Cl ₂	300	27.4
2	B-1	3.0	EtOAc	300	15
3	B-1	2.0	CH ₃ CN	300	71
4	B-1 ^c	3.0	CH ₃ CN	300	0
5	B-1	3.0	CH ₃ CN	0	Trace
6	B-2	2.0	CH ₃ CN	300	80
7	None	3.0	CH ₃ CN	300	8
8	Ru(bpy) ₃ Cl ₂	3.0	CH ₃ CN	300	43

^{*a*} *Reaction conditions*: **1** (0.10 mmol), **2** (0.8 mmol), photocatalyst catalysis **B-1** or **B-2** (1 mol%), air, 35 W Xe light irradiation ($\lambda > 385$ nm), (MeCN)₄CuPF₆ (10 mol%), and solvent (2.0 mL), rt. ^{*b*} Yield of the isolated product. ^{*c*} Without (MeCN)₄CuPF₆.

The scope of both the tetrahydroisoquinoline and the phenylalkynes was extended (Table 6). Phenyl alkynes with electronneutral, electron-withdrawal or electron-donating substituents gave satisfactory yields. Different substitutions on the N-atom of tetrahydroisoquinoline did not hamper the coupled photocatalytic-Cu(1) catalytic reaction.

3.6 Mechanism studies

The mechanism of the photocatalytic reactions was studied using electron spin resonance (ESR) spectroscopy (Fig. 3). 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 was responsible for initiation of the photocatalytic cycles. Observation of the superoxide anion radical (O_2^{-}) supports this putative mechanism.11,38-40 With the new photocatalysts B-1 and B-2, however, it was necessary to confirm the photocatalytic mechanism. The reaction mechanism was studied with ESR spectroscopy (Fig. 3). DMPO and 2,2,6,6-tetramethylpiperidine (TEMP) were used as scavengers for O_2 .⁻ and 1O_2 , respectively.15,40 With DMPO, the ESR signal attributed to its adduct with O2^{•-} was detected for the mixture of B-1 and substrate 1 upon photoirradiation (Fig. 3(b)), but the signal was much weaker in the absence of amine substrate 1a, indicating that electron transfer from the substrate to B-1 was crucial for formation of O_2 . The experiment with TEMP showed that ${}^{1}O_2$ was produced with B-1 in the absence of substrate (1a) (Fig. 3(c)). With the addition of the substrate 1a no ESR signal due to ¹O₂ was detected, indicating that production of ¹O₂ was completely inhibited by electron transfer from substrate 1a to B-**1** (Fig. 3(d)). The electron transfer from the amine substrate to the organic triplet photosensitizer was thus confirmed.

The proposed mechanism is presented in Scheme 2. When the Bodipy-iodo-aza-Bodipy triad (B-2) was photoirradiated with broadband white light from a xenon lamp, the Bodipy singlet excited state (¹Bod*) and iodo-aza-Bodipy singlet excited state (¹AzaBod*) were produced. ¹Bod* is able to transfer the energy to the AzaBod state by the RET process. ³AzaBod* is then populated by ISC. Electron transfer from the tetrahydroisoquinoline substrate to ³AzaBod* produces an Azabod anion and the highly reactive iminium species of the tetrahydroisoquinoline. The Azabod anion returns to the ground state by transferring an electron to O_2 , and $O_2^{\cdot-}$ is then produced. $O_2^{\cdot-}$ can capture two protons from the tetrahydroisoquinoline substrate cation to form a zwitterion and H₂O₂. This mechanism is supported by ¹H NMR (see ESI, Fig. S56[†]). The zwitterion species reacts with maleic anhydride derivatives, and is then oxidized by NBS to produce the target molecules.

The dual catalysis mechanism was also studied using ESR and NMR. We proposed that the electron transferred from the tetrahydroisoquinoline substrate to the organic triplet photosensitizer, then Cu(t) catalyzed the coupled reaction between the iminium species of the tetrahydroisoquinoline and phenylalkyne derivatives (for detailed measurements, see ESI, Scheme S1[†]).

Table 6Scope of the photooxidation-alkynylation reaction catalyzed by B-1 and $B-2^a$

\bigcirc		H R Visible I Solven (MeCN)4 Photoset	ight ts CuPF ₆ nsitizers		H Visible ligt Solvents (MeCN) ₄ Ct Photosensit	nt JPF6 izers	
1:	a	2	₩ 4 R	1b	2	Ŕ	
Entry	Substrate		Product	t^{b} [h] (B-1/B-2)	$\text{Yield}^{c} \left(\textbf{B-1/B-2}\right)$	TON ^d	TOF ^e /min
1	1a	2a	EtOOC N 4a	2/2	59/61	59/61	0.49/0.51
2	F 1a	-√_>-== 2b	EtOOC	3/3	49/53 ^f	49/53	0.27/0.29
3	H₃C 1a	o-√ 2c		4/4	52/55 ^f	52/55	0.22/0.23
4	OH 1a	c-√_>_= 2d	EtOOC	4/4	53/57	53/57	0.22/0.24
5	1b	⟨ 2a		2/2	71/80	71/80	0.59/0.67
6 ^g	F- 1b	-{	→ → −F → −F	4/4	67/73	67/73	0.28/0.30
7	- 1b	-<		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** (1 mol%) and (MeCN)₄CuPF₆ (0.01 mmol) were mixed in CH₃CN (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).

4. Conclusions

Bodipy-iodo-aza-Bodipy triad and iodo-aza-Bodipy triplet photosensitizers have been assessed as photocatalysts in

photoredox organic reactions. These differ from conventional photocatalysts, such as $Ru(bpy)_3Cl_2$, Eosin Y or Rose Bengal, which contain only a single visible light-harvesting unit, in showing strong absorption in the visible spectral region.



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 (0.10 M); (d) B-2 (4.0×10^{-4} M), TEMP (0.10 M); (d) B-2 (4.0×10^{-4} M), TEMP (0.10 M), 1a (5.0×10^{-2} M). In air-saturated CH₃CN. All irradiations were performed at 22 °C for 120 s under a 635 nm continuous laser (210 mW cm⁻²).

Furthermore, the triad shows strong broadband absorption within the range 400–750 nm. Both compounds show high singlet oxygen quantum yields, indicating efficient ISC. They have been used as novel photocatalysts for two photoredox catalytic organic reactions with tetrahydroisoquinilines as substrates for preparing highly functionalized organic compounds *via* the tandem [3 + 2] cycloaddition–aromatization reaction, as well as in Cu(1)-catalyzed alkynylation reactions. We found that the triad photocatalyst, with broadband visible light absorption, was more efficient than the monochromophore photocatalyst, 2,6-diiodo-aza-Bodipy. Furthermore, the iodo-aza-Bodipy was more efficient than conventional photocatalysts such as $[Ru(bpy)_3]Cl_2$. These results will be valuable in the design of efficient organic triplet View Article Online

photosensitizers as photocatalysts for improving photoredox catalytic reactions.

Acknowledgements

We are grateful for financial support to a number of organizations, including the Royal Society (UK) and NSFC (21073028, 21273028 and the China–UK Cost-Share Science Networks, 21011130154), the Ministry of Education (SRFDP– 20120041130005), the Program for Changjiang Scholars, the Innovative Research Team in University (IRT_13R06), the State Key Laboratory of Fine Chemicals (KF1203), Fundamental Research Funds for the Central Universities (DUT14ZD226) and Dalian University of Technology (DUT2013TB07).

References

- 1 C. K. Prier, D. A. Rankic and D. MacMillan, *Chem. Rev.*, 2013, **113**, 5322–5363.
- 2 Y. Xi, H. Yi and A. Lei, Org. Biomol. Chem., 2013, 11, 2387-2404.
- 3 S. Fukuzumi and K. Ohkubo, Chem. Sci., 2013, 4, 561-574.
- 4 D. Ravelli, M. Fagnoni and A. Albini, *Chem. Soc. Rev.*, 2013, **42**, 97–113.
- 5 L. Shi and W. Xia, Chem. Soc. Rev., 2012, 41, 7687-7697.
- 6 J. Xuan and W. Xiao, Angew. Chem., Int. Ed., 2012, 51, 6828-6838.
- 7 A. Berlicka and B. Konig, *Photochem. Photobiol. Sci.*, 2010, 9, 1359–1366.
- 8 C. Streb, Dalton Trans., 2012, 41, 1651-1659.
- 9 Y. Yasu, T. Koike and M. Akita, Org. Lett., 2013, 15, 2136–2139.
- 10 S. Maity, M. Zhu, R. S. Shinabery and N. Zheng, Angew. Chem., Int. Ed., 2012, 51, 222–226.
- 11 Y. Zou, L. Lu, L. Fu, N. Chang, J. Rong, J. Chen and W. Xiao, Angew. Chem., Int. Ed., 2011, 50, 7171–7175.



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

- 12 J. Zhong, Q. Meng, G. Wang, Q. Liu, B. Chen, K. Feng, C.-H. Tung and L. Wu, *Chem.-Eur. J.*, 2013, **19**, 6443-6450.
- 13 G. Zhao, C. Yang, L. Guo, H. Sun, C. Chen and W. Xia, *Chem. Commun.*, 2012, **48**, 2337–2339.
- 14 S. Zhu, A. Das, L. Bui, H. Zhou, D. P. Curran and M. Rueping, J. Am. Chem. Soc., 2013, 135, 1823–1829.
- 15 Q. Liu, Y. Li, H. Zhang, B. Chen, C.-H. Tung and L. Wu, *Chem.-Eur. J.*, 2012, **18**, 620–627.
- 16 D. P. Hari and B. Konig, Org. Lett., 2011, 13, 3852-3855.
- 17 D. P. Hari, T. Hering and B. Konig, *Org. Lett.*, 2012, **14**, 5334–5337.
- 18 T. Xiao, X. Dong, Y. Tang and L. Zhou, *Adv. Synth. Catal.*, 2012, **354**, 3195–3199.
- 19 D. P. Hari, P. Schroll and B. Konig, *J. Am. Chem. Soc.*, 2012, 134, 2958–2961.
- 20 M. Majekz and A. Wangelin, *Chem. Commun.*, 2013, **49**, 5507–5509.
- 21 J. Zhao, S. Ji, W. Wu, W. Wu, H. Guo, J. Sun, H. Sun, Y. Liu, Q. Li and L. Huang, *RSC Adv.*, 2012, 2, 1712–1728.
- 22 A. Kamkaew, S. H. Lim, H. B. Lee, L. V. Kiew, L. Y. Chung and K. Burgess, *Chem. Soc. Rev.*, 2013, **42**, 77–88.
- 23 J. Zhao, W. Wu, J. Sun and S. Guo, *Chem. Soc. Rev.*, 2013, 42, 5323–5351.
- 24 J. Narayanam and C. Stephenson, *Chem. Soc. Rev.*, 2011, **40**, 102–113.
- 25 L. Huang, J. Zhao, S. Guo, C. Zhang and J. Ma, *J. Org. Chem.*, 2013, **78**, 5627–5637.
- 26 L. Huang, X. Cui, B. Therrien and J. Zhao, *Chem.-Eur. J.*, 2013, **19**, 17472–17482.

- 27 S. Guo, L. Ma, J. Zhao, B. Kucukoz, A. Karatay, M. Hayvali, H. G. Yaglioglu and A. Elmali, *Chem. Sci.*, 2014, 5, 489–500.
- 28 M. Rueping, R. M. Koenigs, K. Poscharny, D. C. Fabry, D. Leonori and C. Vila, *Chem.-Eur. J.*, 2012, **18**, 5170–5174.
- 29 G. Ulrich, R. Ziessel and A. Harriman, *Angew. Chem., Int. Ed.*, 2008, **47**, 1184–1201.
- 30 R. Ziessel and A. Harrimanb, *Chem. Commun.*, 2011, 47, 611–631.
- 31 A. Gorman, J. Killoran, C. O'Shea, T. Kenna, W. M. Gallagher and D. F. O'Shea, J. Am. Chem. Soc., 2004, **126**, 10619–10631.
- 32 J. Cao, C. Zhao, P. Feng, Y. Zhang and W. Zhu, *RSC Adv.*, 2012, **2**, 418–420.
- 33 N. Adarsh, M. Shanmugasundaram, R. R. Avirah and D. Ramaiah, *Chem.-Eur. J.*, 2012, **18**, 12655–12662.
- 34 N. Adarsh, R. R. Avirah and D. Ramaiah, *Org. Lett.*, 2010, **12**, 5720–5723.
- 35 S. Kolemen, O. A. Bozdemir, Y. Cakmak, G. Barin, S. Erten-Ela, M. Marszalek, J. Yum, S. M. Zakeeruddin, M. K. Nazeeruddin, M. Gratzelc and E. U. Akkaya, *Chem. Sci.*, 2011, 2, 949–954.
- 36 M. E. El-Khouly, A. N. Amin, M. E. Zandler, S. Fukuzumi and F. D'Souza, *Chem.–Eur. J.*, 2012, **18**, 5239–5247.
- 37 M. Yuan, X. Yin, H. Zheng, C. Ouyang, Z. Zuo, H. Liu and Y. Li, *Chem.-Asian J.*, 2009, 4, 707–713.
- 38 L. Huang and J. Zhao, Chem. Commun., 2013, 49, 3751-3753.
- 39 S. Guo, H. Zhang, L. Huang, Z. Guo, G. Xiong and J. Zhao, *Chem. Commun.*, 2013, 49, 8689–8691.
- 40 L. Huang and J. Zhao, RSC Adv., 2013, 3, 23377–23388.