CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.201302492

Energy-Funneling-Based Broadband Visible-Light-Absorbing Bodipy–C_{60} Triads and Tetrads as Dual Functional Heavy-Atom-Free Organic Triplet Photosensitizers for Photocatalytic Organic Reactions

Ling Huang,[a] Xiaoneng Cui,[a] Bruno Therrien,[b] and Jianzhang Zhao*[a]

Abstract: C_{60}–bodipy triads and tetrads based on the energy-funneling effect that show broadband absorption in the visible region have been prepared as novel triplet photosensitizers. The new photosensitizers contain two or three different light-harvesting antennae associated with different absorption wavelengths, resulting in a broad absorption band (450–650 nm). The panchromatic excitation energy harvested by the bodipy moieties is funneled into a spin converter (C_{60}), thus ensuring intersystem crossing and population of the triplet state. Nanosecond time-resolved transient absorption and spin density analysis indicated that the T_1 state is localized on either C_{60} or the antennae, depending on the T_1 energy levels of the two entities. The antenna-localized T_1 state shows a longer lifetime ($\tau_T = 132.9\ \mu s$) than the C_{60}-localized T_1 state (ca. 27.4 μs). We found that the C_{60} triads and tetrads can be used as dual functional photocatalysts, that is, singlet oxygen ($^1O_2$) and superoxide radical anion ($O_2^{\bullet -}$) photosensitizers. In the photooxidation of naphthol to juglone, the $^1O_2$ photosensitizing ability of the C_{60} triad is a factor of 8.9 greater than the conventional triplet photosensitizers tetraphenylporphyrin and methylene blue. The C_{60} dyads and triads were also used as photocatalysts for $O_2^{\bullet -}$-mediated aerobic oxidation of aromatic boronic acids to produce phenols. The reaction times were greatly reduced compared with when [Ru(bpy)$_3$Cl$_2$] was used as photocatalyst. Our study of triplet photosensitizers has shown that broadband absorption in the visible spectral region and long-lived triplet excited states can be useful for the design of new heavy-atom-free organic triplet photosensitizers and for the application of these triplet photosensitizers in photo-organocatalysis.

Keywords: fullerenes · photochemistry · photooxidation · sensitizers · UV/Vis spectroscopy

Introduction

Triplet photosensitizers are widely used in photocatalytic organic reactions,[1,2] photovoltaics,[3] photodynamic therapy,[4–10] and triplet–triplet annihilation (TTA) upconversion.[11–15] Triplet photosensitizers usually contain heavy atoms such as Pt^{II}, Ir^{III}, or iodine.[1,2,9,14,15] The heavy-atom effect facilitates intersystem crossing (ISC), which produces a triplet excited state.[9,10,16] However, it is difficult to populate the triplet state of organic chromophores lacking heavy atoms.[8f,9,16] Derivatization of a known fluorophore, a popular strategy for preparing new fluorescent molecules, is not applicable for the design of new organic triplet photosensitizers because subtle derivatizations of a known organic triplet photosensitizer may eliminate completely the ISC.[9f,16] Therefore it would be highly desirable to develop a general molecular structure for heavy-atom-free organic triplet photosensitizers that can be easily functionalized with a predictable ISC effect. This goal remains a significant challenge in photochemistry.

All current triplet photosensitizers are based on monochromophores.[4,5,8–10,17] These photosensitizers possess only one major absorption band in the visible region, thus covering only a small part of the visible spectral range. This is detrimental to photocatalysis with panchromatic light excitation, such as with solar light. Triplet photosensitizers with panchromatic or broadband absorption have not been reported,[9c,10,17] although this kind of photosensitizer can efficiently harvest panchromatic light excitation. To address a similar problem, molecular dyads or triads that exhibit intramolecular energy funneling (such as fluorescence resonance energy transfer, FRET) have been used in fluorescent molecular arrays.[18–20] However, to the best of our knowledge, this strategy has never been used with triplet photosensitizers to access broadband absorption in the visible range.

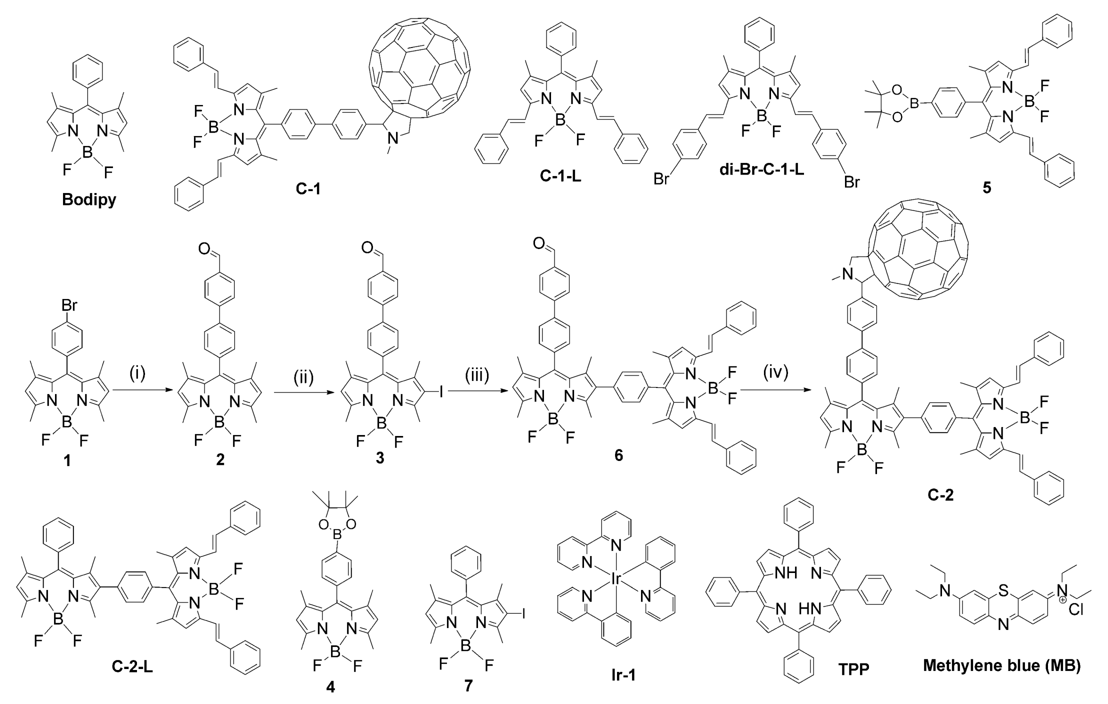
To overcome the aforementioned challenges, and inspired by the seminal work of $^1O_2$ photosensitization by an intramolecular energy transfer approach using porphyrin as the energy acceptor and a two-photon-absorbing chromophore as the antenna,[21] herein we report C_{60}–bodipy triads and

---

[a] L. Huang, X. Cui, Prof. J. Zhao
State Key Laboratory of Fine Chemicals
E-208, West Campus
Dalian University of Technology
Dalian 116024 (P.R. China)
Fax: (+86) 411-8498-6236
E-mail: zhaojzh@dlut.edu.cn

[b] Prof. B. Therrien
Institute of Chemistry, University of Neuchâtel
Avenue de Bellevaux 51, 2000 Neuchâtel (Switzerland)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201302492.



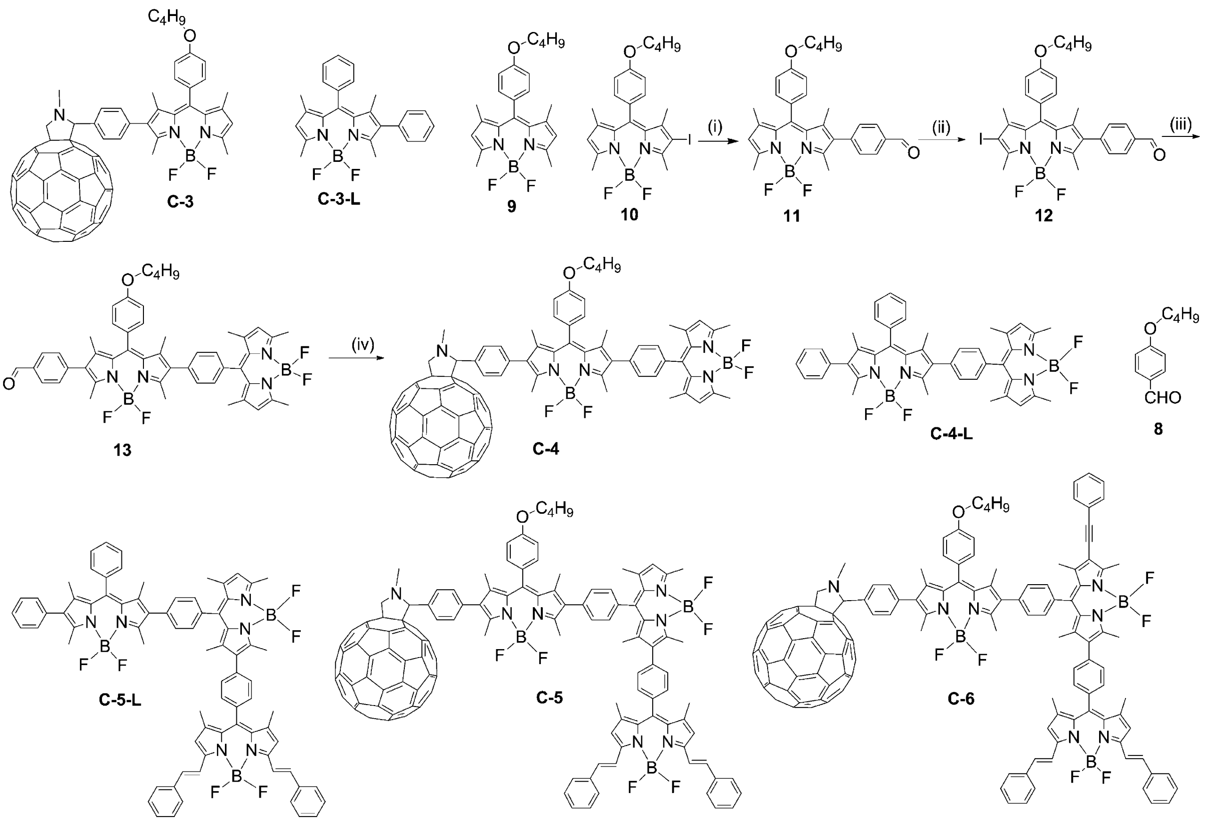
Scheme 1. Synthesis of triad **C-2** and the reference compounds. The model triplet photosensitizers [Ir(ppy)$_2$bpy][PF$_6$] (**Ir-1**), tetraphenylporphyrin (TPP) and methylene blue (MB) are also shown. Reagents and conditions: (i) 4-OHCC$_6$H$_4$B(OH)$_2$ (0.6 mmol), 5 mol% [Pd(PPh$_3$)$_4$], 3 equiv K$_2$CO$_3$, toluene/ethanol/water, 2:2:1, v/v, reflux, 8 h, 85%; (ii) 1 equiv *N*-iodosuccinimide (NIS), RT, 61%; (iii) **5** (prepared from **4**, for this and other procedures, see the Supporting Information), 5 mol% [Pd(PPh$_3$)$_4$], 3 equiv K$_2$CO$_3$, toluene/ethanol/water, 2:2:1, v/v, reflux, 8 h, 66%; (iv) 4.0 equiv *N*-methylglycine, C$_{60}$, in toluene, reflux, 12 h, 73%.

tetrads as heavy-atom-free triplet photosensitizers that show broadband absorption in the visible range (Schemes 1 and 2). These photosensitizers are based on a multiple intramolecular energy funneling effect from the antennae to the C$_{60}$ unit. In addition, and without the presence of any heavy atoms, the triplet excited states of the triads and tetrads are populated upon photoexcitation. Furthermore, we found that the compounds can be used as dual functional photoredox catalysts in various photocatalytic reactions, such as ^{1}O$_2$- and O$_2^{\bullet-}$-mediated photocatalytic reactions. In the photocatalytic oxidative coupling reactions of amines, the new triplet photosensitizers are a factor of 8.9 more efficient as singlet oxygen (^{1}O$_2$) photosensitizers than conventional triplet photosensitizers based on a monochromophore, such as tetraphenylporphyrin (TPP) or methylene blue (MB). Furthermore, in the photocatalytic oxidation of aromatic boronic acids to produce functionalized phenols (via O$_2^{\bullet-}$ photosensitization), the reaction time was reduced to less than 4 h from the previously reported 69–96 h required with a conventional Ru$^{\text{II}}$–polyimine photocatalyst, and good functional group tolerance was found for the O$_2^{\bullet-}$-mediated photooxidation of arylboronic acids. These results will be useful for the future development of efficient triplet photosensitizers, the photochemistry of fullerenes, and the application of C$_{60}$–organic hybrids as photocatalysts in various photocatalytic reactions.

Results and Discussion

Design and synthesis of C$_{60}$–bodipy triplet photosensitizers: The molecular design is based on the ISC capability of C$_{60}$.[22] However, C$_{60}$ itself is not an ideal triplet photosensitizer because of its weak absorption in the visible region. Therefore light-harvesting antennae were attached to C$_{60}$ to enhance its absorption.[22–31] Previously, C$_{60}$ compounds with strong visible-light or panchromatic absorption have been prepared, but their triplet-state populations and photocatalytic properties have not been reported.[23–26] In this work, bodipy was selected as an antenna due to its versatile derivatization and satisfactory photophysical properties.[24,32,33] Intramolecular energy transfer from the bodipy antenna to C$_{60}$ is expected, which in return produces a triplet excited state of C$_{60}$.[30a,31,34–38] To broaden the absorption band of C$_{60}$ molecular arrays in the visible spectral range, multichromophores of styryl-bodipy, 2-phenyl-bodipy, or ethynylated bodipy units were used to construct triads and tetrads (Schemes 1 and 2). These C$_{60}$–bodipy hybrids give broad absorption bands in the range 450–650 nm.[39,40] Dyad **C-1** and triad **C-2** were prepared in moderate yields from bromobodipy and C$_{60}$ (Scheme 1 and the Supporting information) and one to three bodipy units were used for the preparation of dyad **C-3**, triad **C-4**, and tetrads **C-5** and **C-6** (see Scheme 2).

The weak absorption of C$_{60}$ in the visible range ($\varepsilon <$ 200 $\text{M}^{-1}\text{cm}^{-1}$ beyond 500 nm) does not deny the efficient in-



Scheme 2. Structures of C_{60}-bodipy tetrads **C-5** and **C-6** and the reference compounds. Reagents and conditions: (i) 2 equiv 4-formylphenylboronic acid, 5 mol% [Pd(PPh$_3$)$_4$], 3 equiv K_2CO_3, toluene/ethanol/water, 2:2:1, v/v, reflux, 8 h, 82%; (ii) RT, 2 equiv NIS, 95%; (iii) 1.2 equiv compound 4, 5 mol% [Pd(PPh$_3$)$_4$], 3 equiv K_2CO_3, toluene/ethanol/water, 2:2:1, v/v, reflux, 8 h, 68%; (iv) 4.0 equiv *N*-methylglycine, C_{60}, reflux, 12 h, toluene, 66%. For detailed procedures, see the Supporting Information.

tramolecular energy transfer from the bodipy antenna to the C_{60} unit. The weak absorption of C_{60} at 500–700 nm is due to symmetry-forbidden $S_0 \rightarrow S_n$ transitions,[25] which do not occur in intramolecular energy transfer from an antenna to the intramolecular energy acceptor C_{60}.

UV/Vis absorption and fluorescence emission spectra: The UV/Vis absorption spectra of the dyad **C-3** and triad **C-2**, as well as the reference compounds bodipy and C_{60} were recorded in toluene (Figure 1). In comparison with C_{60}, dyad **C-3** shows a strong absorption at 517 nm ($\varepsilon = 76\,000\,\text{M}^{-1}\text{cm}^{-1}$), which can be attributed to the bodipy antenna (Figure 1a). Similarly, triad **C-2** shows a strong absorption band at 517 nm ($\varepsilon = 61\,000\,\text{M}^{-1}\text{cm}^{-1}$) with a second absorption band at 629 nm ($\varepsilon = 83\,000\,\text{M}^{-1}\text{cm}^{-1}$). These two absorption bands can be attributed to the bis-bodipy antenna in which two different chromophores exist (**C-2-L** is the reference compound for the antennae in **C-2**). As a reference, the C_{60}–styryl dyad **C-1** was prepared and, as expected, it shows only one strong absorption band centered at 629 nm.[38b] The broader absorption band of triad **C-2** relative to dyad **C-1** is beneficial for the application of C_{60}–bodipy arrays as broadband light-absorbing triplet photosensitizers. Similar absorption profiles were observed for the triad **C-4** and the tetrads **C-5** and **C-6** (see Figure S64 in the Supporting Information).

The fluorescent properties of the triads were also studied (Figure 2 and the Supporting Information).[31] The emission

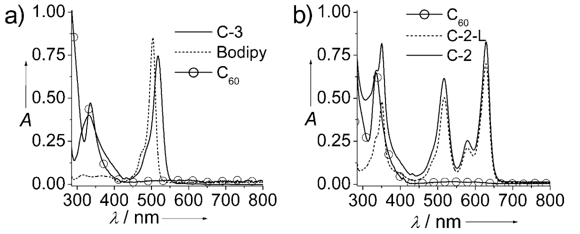


Figure 1. a) UV/Vis absorption spectra of C_{60}, bodipy, and the C_{60}–bodipy dyad **C-3**. b) UV/Vis absorption spectra of C_{60} and C_{60}–bodipy triads **C-2** and **C-2-L** (toluene, 1.0×10^{-5} M, 20 °C).

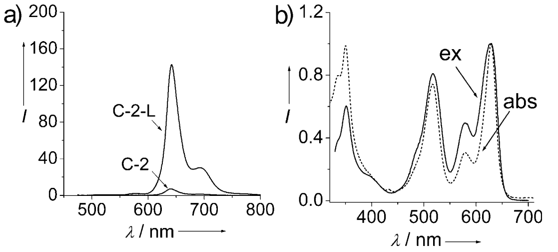


Figure 2. a) Fluorescence spectra of **C-2** and **C-2-L** ($\lambda_{ex} = 470$ nm). b) Fluorescence excitation ($\lambda_{em} = 640$ nm) and UV/Vis absorption spectra of **C-2** (toluene, 1.0×10^{-5} M, 20 °C).

of the antenna was significantly quenched in **C-2** (Figure 2a), otherwise the styryl-bodipy antenna in **C-2** would show fluorescence emission similar to **C-2-L**. The quenching of the emission band at 628 nm in the triad is due to intramolecular energy transfer from the antenna to the C_{60} unit. Intramolecular electron transfer from the antenna to C_{60} may also be responsible for the quenching effect.[30a,31] The efficient intramolecular energy transfer in **C-2** is based on the higher energy of the S_1 state of **C-2-L** (approximated to be 1.94 eV by the fluorescence emission of **C-2-L** at 640 nm) in comparison with the S_1 state of the C_{60} unit (720 nm, 1.72 eV).[30a] Figure 2a also indicates that the emission of the bodipy unit (at ca. 500 nm) is completely quenched in **C-2-L**, which indicates efficient energy transfer in **C-2-L**.

Similarly, the emission of the antenna is quenched in dyad **C-3** (see Figure S65). This intramolecular energy transfer ensures that the excitation energy harvested by the antenna in the triads is funneled into the intramolecular energy acceptor, that is, the C_{60} unit.[31] The intramolecular energy transfer is estimated to be 99.5 % in **C-3** and 91.5 % in **C-2**, based on the fluorescence quantum yields.

To confirm the intramolecular energy transfer in the C_{60} dyads and triads, the fluorescence excitation spectra and the UV/Vis absorption spectra of **C-2** were compared and a good match was found for the two spectra (Figure 2b). The spectra of all other compounds are presented in Figures S66–S69 in the Supporting information). These results indicate efficient intramolecular energy transfer to the energy donors of the dyads and triads upon selective excitation.

Nanosecond time-resolved transient difference absorption of the triplet photosensitizers (localization of the T_1 state): To prove the populations of the triplet excited states of the dyads and triads, nanosecond time-resolved transient difference absorption spectra of the dyads, triads, and tetrads were recorded, the results being exemplified with dyad **C-3** and triad **C-2** (Figure 3). A transient absorption (TA) band at 720 nm was observed for **C-3**, which is the feature absorption of the T_1 state of C_{60}. Furthermore, bleaching of the steady-state absorption of bodipy was not observed (Figure 3a). Therefore the TA band at 720 nm can be assigned to the C_{60} localized triplet state, the lifetime of the triplet state being 27.4 μs.

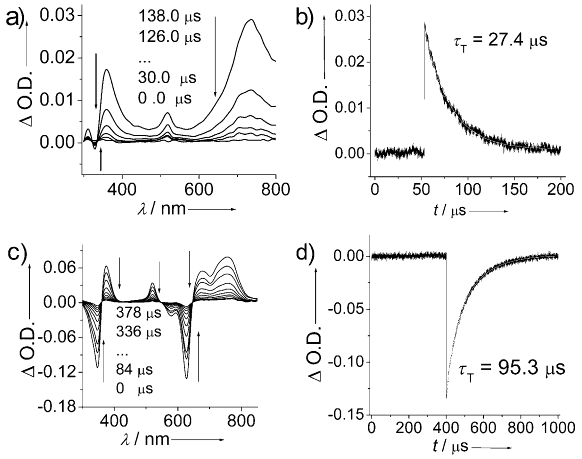


Figure 3. Nanosecond time-resolved transient difference absorption spectra of **C-3** and **C-2**. a) Transient difference absorption spectra of **C-3**. b) Decay of **C-3** at 720 nm. c) Transient difference absorption spectra of **C-2**. d) Decay of **C-2** at 630 nm. $\lambda_{ex} = 532$ nm (in deaerated toluene, 1.0×10^{-5} M, 20 °C).

Upon pulsed excitation at 532 nm, bleaching at 345 and 629 nm was observed for **C-2** (Figure 3c) due to ground-state absorption of the styryl-bodipy antenna (**C-1-L** moiety, see Figure S71 in the Supporting Information).[38] Interestingly, bleaching of the bodipy part was not observed (ca. 517 nm, Figure 1b). These results indicate that the triplet excited state is localized on the styryl-bodipy unit due to the backward triplet energy transfer from C_{60} to styryl-bodipy. As a result, the **C-2** molecule in the ground state is depleted and bleaching bands are observed in the TA of **C-2** at the position that the styryl-bodipy antenna gives steady-state absorption (347 and 628 nm, similarly to the absorption of **C-1-L**). Such "ping-pong" energy transfer has previously been reported for C_{60} dyads.[31,38] The assignment of the triplet excited state of the dyad to the styryl-bodipy-localized triplet excited state is supported by the similarities between the transients of the triad and the reference compound **di-Br-C-1-L** (Scheme 1 and Figure S72). The lifetime of the T_1 excited state of **C-2** was determined to be 95.3 μs (Figure 3), which is much longer than that of C_{60} (ca. 40.0 μs),[26] which also confirms that the T_1 state is not localized on C_{60}.

The long-lived triplet excited state is in agreement with the postulated styryl-bodipy-localized triplet excited state. Similar long-lived triplet excited states were observed for other C_{60} dyads and triads (see Figures S74–S77 in the Supporting Information). For example, a styryl-bodipy-localized triplet excited state lifetime of 132.3 μs was observed for **C-6** (Table 1 and Figure S76). In general, the antenna-localized triplet state shows a much longer lifetime than the C_{60}-localized triplet state (Table 1). This observation may be useful for the design of new triplet photosensitizers with long-lived triplet excited states, which is crucial for the application of triplet photosensitizers in triplet–triplet energy-transfer (TTET) processes.[18] TTET processes can be enhanced with triplet photosensitizers that show long-lived triplet excited states. TTETs are widely involved in singlet oxygen ($^1O_2$) photosensitization[10] and triplet–triplet annihilation (TTA) upconversion.[11–15,17]

Spin density surfaces of the triplet photosensitizers (localization of the triplet state): The localization of the triplet excited states of the dyads, triads, and tetrads was also confirmed by a theoretical approach, that is, by analysis of the spin density surfaces (Figure 4).[38]

For **C-3**, the spin density is exclusively localized on the C_{60} unit, which is in full agreement with the corresponding transient absorption spectra (Figure 3a). The calculation indicates that the spin density of **C-2** is exclusively distributed

Table 1. Photophysical parameters of the C_{60} dyads, triads, and tetrads, reference compounds, and C_{60}.[a]

	λ_{abs} [nm]	ε [$10^5\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$]	λ_{em} [nm]	Φ_L[b]	ET_{eff} [%][d]	τ_T[e] [µs]	τ_F[f] [ns]	Localization of T_1 state
bodipy	503	0.85	517	0.83	–[g]	–[g]	3.6	–[g]
C-1-L	355/628	0.87/1.24	642	0.59	–[g]	–[g]	4.6	–[g]
C-2-L	517/579/629	0.50/0.21/0.70	639	0.47	99.9	–[g]	4.5	–[g]
C-3-L	517	0.94	540	0.79[c]	–[g]	–[g]	4.3	–[g]
C-4-L	504/532	0.93/0.70	558	0.75[c]	–[g]	–[g]	4.0	–[g]
C-5-L	351/522/578/629	0.48/0.74/0.20/0.65	641	0.61	97.2	–[g]	4.4	–[g]
C-1	630	0.64	643	0.01	98.3	71.2	–[g]	sty-bodipy
C-2	517/579/629	0.61/0.25/0.83	640	0.04	91.5	95.3	–[g]	sty-bodipy
C-3	517	0.76	535	0.004	99.5	27.4	–[g]	C_{60}
C-4	504/532	1.17/0.98	558	0.004	99.5	27.0	–[g]	C_{60}
C-5	336/350/523/578/629	0.99/1.25/0.32/1.02/0.79	641	0.14	77.1	104.5	1.6	sty-bodipy
C-6	350/535/628	0.54/0.68/0.65	640	0.12	–[g]	132.3	1.5	sty-bodipy
C_{60}	335	0.65		0.001	–[g]	40.0	–[g]	C_{60}

[a] Recorded in toluene at 20°C. [b] With **C-1-L** (Scheme 1, $\Phi=0.59$ in toluene) as standard. For **C-1-L**, **C-2-L**, **C-5-L**, **C-1**, **C-2**, **C-5**, and **C-6**, excitation at 590 nm. [c] With BOD (Scheme 1, $\Phi=0.72$ in THF) as standard. Excitation at 500 nm for **C-3-L**, **C-4-L**, **C-3**, and **C-4**. [d] ET_{eff} is the energy transfer efficiency. Calculated by fluorescence quantum yield $ET_{eff}=1-\tau/\tau_0$. [e] Triplet excited state lifetimes. Measured by nanosecond transient absorption in deaerated solutions. [f] Fluorescence lifetimes. [g] Not applicable.

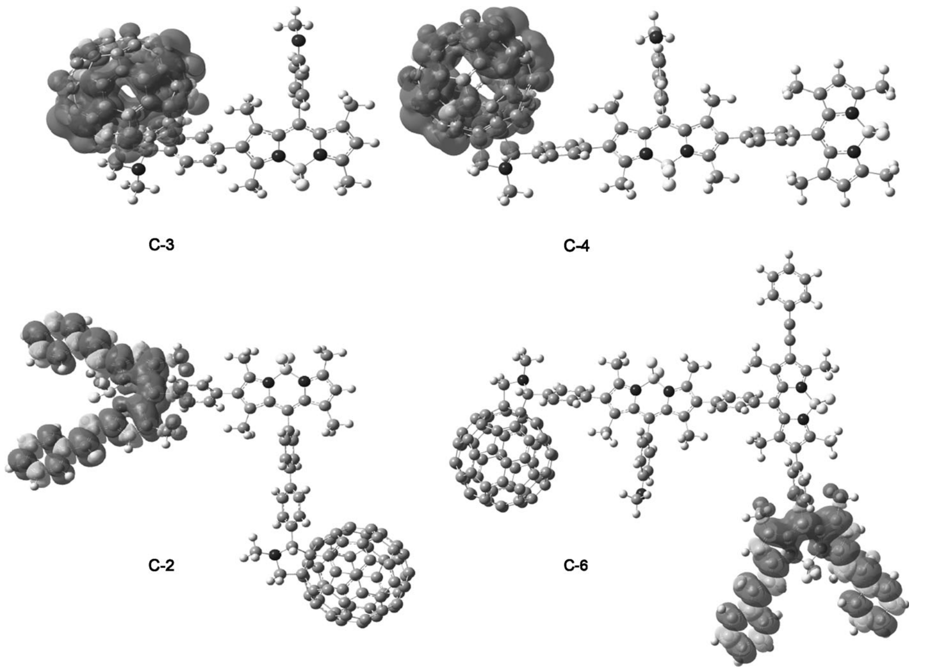
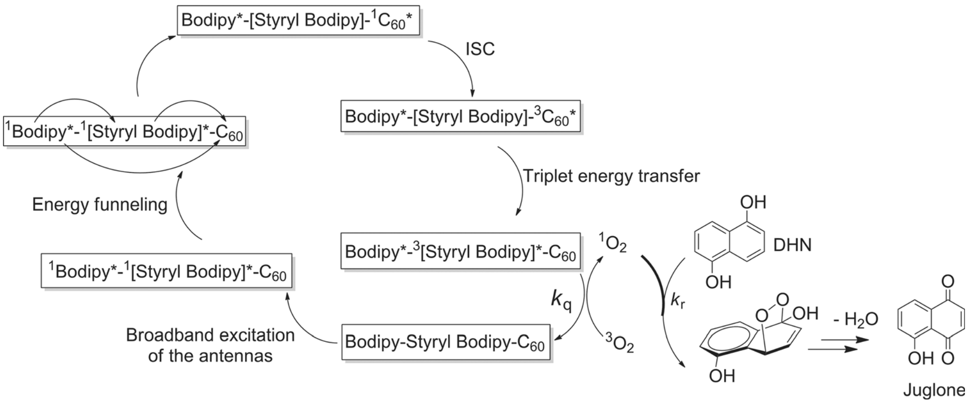


Figure 4. Images of the spin density of dyad **C-3**, triads **C-2** and **C-4**, and tetrad **C-6**. Calculations were performed at the B3LYP/6-31G(d) level of theory with Gaussian 09W based on the optimized triplet-state geometry.

on the styryl-bodipy unit, the C_{60} and other bodipy unit not contributing to the spin density surface. This spin density analysis is also in full agreement with the time-resolved transient difference absorption spectrum of the triad (Figure 3c). The spin densities of **C-4** and **C-6** were also studied (Figure 4), the results also being in full agreement with the TA spectra (see Figures S74– S77 in the Supporting Information).

Evaluation of the singlet oxygen ($^1O_2$) photosensitizing ability of the triplet photosensitizers: To compare the efficiencies of these broadband visible-light-absorbing triplet photosensitizers with conventional monochromophore triplet photosensitizers that show only one absorption band in the visible region, the C_{60} dyads, triads, and tetrads were evaluated as triplet photosensitizers for photooxidation reactions. The singlet oxygen ($^1O_2$) sensitizing ability was studied with 1,5-dihydroxynaphthalene (DHN) as the $^1O_2$ scavenger (Scheme 3) so that the production of the $^1O_2$ could be easily monitored by following the changes in the UV/Vis absorption spectra.[41] The product of this photooxidation, juglone, can be used for the preparation of bioactive compounds.

Previously, Ir^{III} complex photosensitizers were used for the photooxidation of DHN.[41] However, the Ir^{III} complexes show weak absorption in the visible range, which is typical of most of the transition-metal-complex triplet photosensitizers based on a monochromophore profile.[4,7,9,41] Accordingly, C_{60}–chromophore dyads have been used as $^1O_2$ photosensitizers.[29,38] However, none of these C_{60} derivatives contained any visible-light-harvesting antenna, or only one chromophore as a light-harvesting antenna, and thus the UV/Vis absorption bands are either very weak or narrow in the visible range. $^1O_2$ photosensitizers based on fluorescence resonance energy transfer have also been reported, but these photosensitizers are composed of porphyrin as the energy acceptor and of two-



Scheme 3. Photooxidation of DHN with C_{60}–triad **C-2** as the triplet photosensitizer.

photon excitation ligands, that is, the photosensitizers do not show broadband absorption in the visible range.[21]

Herein we have demonstrated that the C_{60}–bodipy triad **C-2**, which shows broadband absorption in the visible range, is an effective combination for efficiently harvesting panchromatic excitation light.

Photooxidation with the C_{60} dyads and triads, as well as with some conventional organic triplet photosensitizers, such as methylene blue (MB) and tetraphenylporphyrin (TPP), were studied (Figure 5 and the Supporting information). Upon photoexcitation, $^1O_2$ was produced and thus DHN was oxidized and juglone was produced. Accordingly, the UV/Vis absorption of DHN at 301 nm decreased and the absorption of juglone at 427 nm increased.[38,41,42]

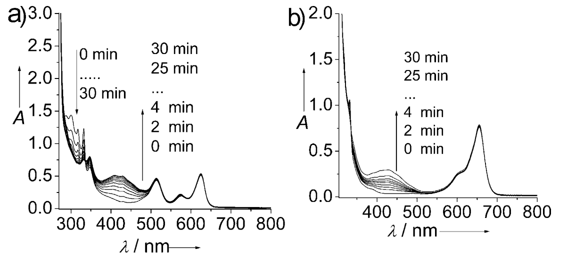


Figure 5. UV/Vis absorption spectral changes observed upon the photooxidation of DHN with a) **C-2** and b) MB as photosensitizers. c[photosensitizers] = 5.0×10^{-6} M, c[DHN] = 2.0×10^{-4} M, light intensity = 20 mW cm^{-2} in CH_2Cl_2/MeOH, 9:1, v/v, 20 °C.

The $^1O_2$ photosensitizing abilities of the photosensitizers were quantitatively compared by plotting $\ln(C_t/C_0)$ (C being the concentration of 1,5-dihydroxylnaphthalene) against the irradiation time (Figure 6). Based on the slopes of the lines, it is clear that the $^1O_2$ sensitizing ability of **C-2** is much stronger than the organic triplet photosensitizers such as TPP and MB with a monochromophore. Furthermore, the $^1O_2$ sensitizing ability of triad **C-2** is much greater than that of dyad **C-1**, which indicates that our strategy of using broadband absorption to enhance the performance of the triplet photosensitizers is successful.

The initial rate constants (ν_i) of the photooxidation reactions were also calculated (Table 2). The ν_i value for triad **C-2** ($\nu_i = 6.2\times10^{-5}\,\mathrm{M}^{-1}\,\mathrm{min}^{-1}$) is a factor of 3.6 greater than that of dyad **C-1** ($\nu_i = 17.2\times10^{-6}\,\mathrm{M}^{-1}\,\mathrm{min}^{-1}$). This clearly demonstrates that the broadband absorption of triad **C-2** is more appropriate for photosensitization than the narrow absorption of monochromophore triplet photosensitizers such as dyad **C-1**. To the best of our knowledge, this is the first time that a heavy-atom-free organic triplet photosensitizer with broadband absorption in the visible range based on a multichromophore has been developed. Similar enhanced photooxidation was also found for compounds **C-4**, **C-5**, and **C-6** (see Figure 6, Table 2, and Figure S80 in the Supporting Information). The photooxidation velocities are generally a factor of 4 to 8.9 greater than those of conventional triplet photosensitizers such as TPP and MB (Table 2). The $^1O_2$ quantum yields (Φ_Δ) of the C_{60}-based triplet photosensitizers are presented in Table 2 and are generally comparable to or even higher than those of conventional organic triplet photosensitizers.

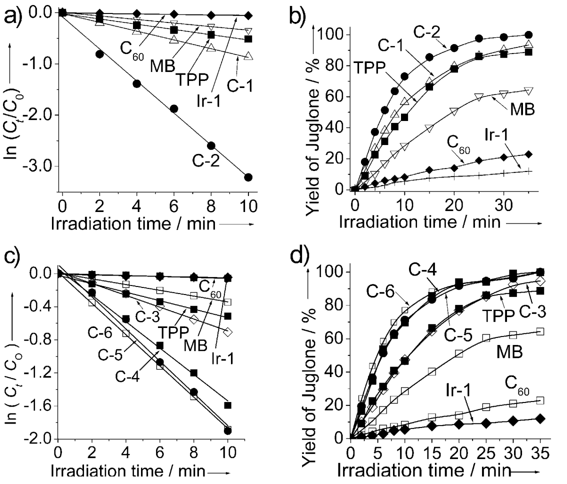


Figure 6. Photooxidation of DHN with different triplet photosensitizers. a,c) Plots of $\ln(C_t/C_0)$ vs. irradiation time (t) for the photooxidation of DHN. b,d) Plots of chemical yield as a function of irradiation time (in CH_2Cl_2/MeOH, 9:1, v/v, 20 °C).

C_{60}–bodipy hybrids as photocatalysts for the aerobic oxidation of aromatic boronic acids to produce phenols by the generation of the superoxide radical anion ($O_2^{\bullet-}$): The application of C_{60}–organic chromophore triplet photosensitizers can be extended to other photocatalytic reactions, such as the aerobic oxidation of boronic acids to produce phenols.[1b] Recently, we used C_{60}–bodipy compounds for a [3+2] addi-

Table 2. Pseudo-first-order kinetic parameters and yields of juglone for the photooxidation of DHN by using C_{60} dyads and triads, as well as some typical conventional organic triplet photosensitizers.[a]

	k_{obs} [min^{-1}][b]	ν_i [10^{-6} M min^{-1}][c]	Φ_Δ[d]	Yield [%][e]
C-1	0.086	17.2	0.82	93.3
C-2	0.31	62.0	0.92	99.9
C-3	0.072	14.4	0.81[f]	94.7
C-4	0.16	32.0	0.87[f]	99.9
C-5	0.19	38.0	0.88	99.9
C-6	0.20	40.0	0.89	99.9
MB	0.035	7.0	0.57	64.5
TPP	0.051	10.2	0.62	88.1
C_{60}	0.006	1.2	0.76	22.1
Ir-1	0.0043	0.8	0.97[g]	12.5

[a] Experiments performed in CH_2Cl_2/MeOH, 9:1 with c[photosensitizers] $= 5.0 \times 10^{-6}$ M and c[DHN] $= 2.0 \times 10^{-4}$ M at 20 °C. [b] Pseudo-first-order-rate constants. [c] Initial rate of DHN consumption. [d] Quantum yield of singlet oxygen ($^1O_2$) determined by using MB as standard ($\Phi_\Delta = 0.57$ in CH_2Cl_2). [e] Yield of juglone after photoirradiation for 35 min. [f] Determined with Rose Bengal (RB) as standard ($\Phi_\Delta = 0.80$ in methanol). [g] Ref. [41].

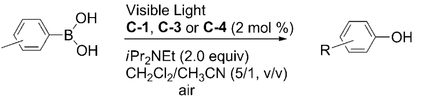
tion/cyclization reaction, but the photocatalyst used showed only one major absorption band in the visible spectral region.[2i] Functionalized phenols are important intermediates for the preparation of pharmaceutical products and several synthetic methods have been developed, but very few rely on photocatalysis.

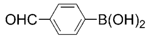
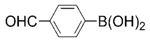
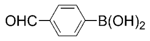
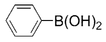
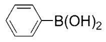
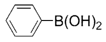
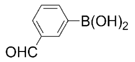
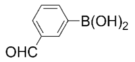
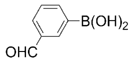
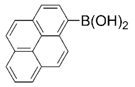
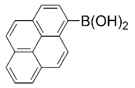
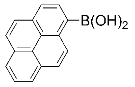
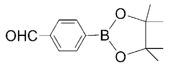
Previously, a Ru^{II}–polyimine complex has been used as a photocatalyst for the aerobic oxidation of aromatic boronic acids.[1b] However, there is much scope for enhancing this environmentally benign and atom economic green synthetic protocol. For example, the reaction time with the [$Ru(bpy)_3Cl_2$] catalyst (69–96 h) needs to be reduced and, more importantly, heavy-atom-free triplet photosensitizers should be used to achieve a greener synthesis.

C_{60} is a well-known electron acceptor, and thus we envisaged that in the presence of a sacrificial electron donor (redox reagent) such as an amine, electron transfer from the amine to the C_{60} dyad will occur and electrons will be conveyed to O_2, and as a result $O_2^{\bullet-}$ will be produced, which can then react with aromatic boronic acids to produce functionalized phenols.[1b]

The photocatalytic properties of the C_{60} dyads and triads for the aerobic oxidation of various aromatic boronic acids were studied (Table 3). The aerobic photooxidation of aromatic boronic acids proceeded smoothly with the triplet photosensitizers **C-1**, **C-3**, and **C-4**. The reactions were complete within 2–4 h, with satisfactory yields of 79–92 %. These reaction times are much shorter than those required with [$Ru(bpy)_3Cl_2$] as the photocatalyst (69–96 h).[1b] Through control experiments, we proved that the C_{60} triplet photosensitizers, the electron donor (N,N-diisopropylethylamine), and photoirradiation are indispensable for the photocatalytic aerobic oxidation (see the Supporting Information). Furthermore, C_{60} alone or the light-harvesting antennae **C-1-L** and **C-4-L** were also used for the photocatalytic reaction, but no product was isolated. This result also suggests that both strong visible-light-harvesting and the production of the triplet excited state are essential for the photocatalytic reactions.

Table 3. Visible-light-induced aerobic oxidative hydroxylation of aryl boronic acids.[a]



Entry	Arylboron species	Catalyst	t [h]	Yield [%][b]
1		**C-1**	3.0	85
2		**C-3**	3.0	87
3		**C-4**	2.5	91
4		**C-1**	4.0	79
5		**C-3**	4.0	81
6		**C-4**	3.0	84
7		**C-1**	3.0	78
8		**C-3**	3.0	83
9		**C-4**	2.0	82
10		**C-1**	3.0	82
11		**C-3**	3.0	84
12		**C-4**	2.0	92
13		**C-3**	4.0	89

[a] Reaction conditions: Boronic acid (0.10 mmol), photocatalyst (2 mol %), iPr_2NEt (2.0 equiv), CH_2Cl_2/CH_3CN, 5:1, v/v (6 mL), 35 W Xe lamp irradiation in air. The reaction was monitored by TLC. [b] Yield of product upon isolation.

The photocatalytic photoreactions show good substrate tolerance (Table 3). For example, 3-formyl- and 4-formylphenylboronic acids gave satisfactory yields of the corresponding phenols. In addition, phenylboronic pinacol ester can also be used successfully as a substrate (entry 13, Table 3). To the best of our knowledge, this is the first time that C_{60}–organic chromophore hybrids showing broadband absorption of visible light have been used as photocatalysts for preparative organic synthesis[1,2] other than for the production of $^1O_2$, which has been known for a long time with C_{60}.[29]

An organic triplet photosensitizer (Acid Red 87, that is, Eosin Y, tetrabromofluorescein sodium salt) has been previously used for the photocatalytic aerobic oxidation of aromatic boronic acids to produce phenols.[1b] However, the reaction time was much longer (96 h).[1b] In this work, with the C_{60}–bodipy hybrids, this reaction time is greatly reduced to less than 4 h (Table 3). To the best of our knowledge this is the first time that heavy-atom-free triplet photosensitizers

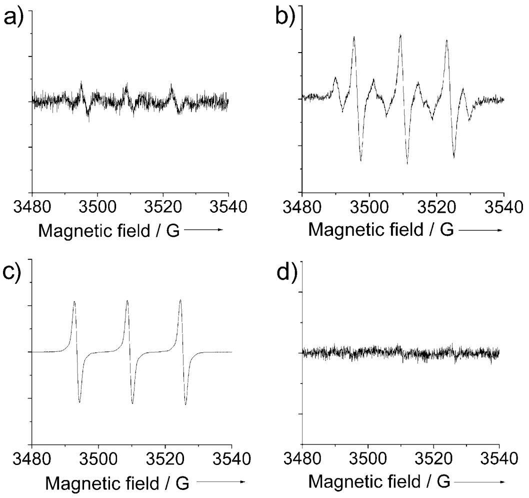
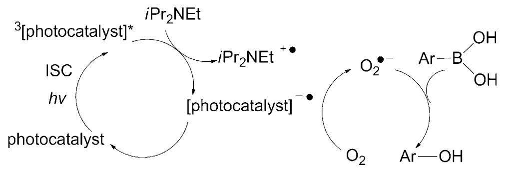


Figure 7. EPR spectra of mixtures of triad **C-4** and radical scavengers to ascertain the photocatalytic mechanism. a) **C-4** (1.0×10^{-5} M) and DMPO (1.0×10^{-2} M), b) **C-4** (1.0×10^{-5} M), *N*,*N*-diisopropylethylamine (3.0×10^{-3} M), and DMPO (1.0×10^{-2} M), c) **C-4** (1.0×10^{-5} M) and TEMP (0.10 M), and d) **C-4** (1.0×10^{-4} M), TEMP (0.10 M), *N*,*N*-diisopropylethylamine (3.0×10^{-3} M) in air-saturated CH_2Cl_2 upon irradiation. All irradiations were performed with a 532 nm laser for 100 s (141 mW cm^{-2}) at 20 °C.

have been used for the photocatalytic aerobic oxidation of aromatic boronic acids to produce phenols. Electron paramagnetic resonance (EPR) experiments confirmed that the photocatalytic aerobic oxidations are mediated by $O_2^{\bullet-}$ (Figure 7). 5,5-Dimethyl-1-pyrroline *N*-oxide (DMPO) and 2,2,6,6-tetramethylpiperidine (TEMP) were employed as scavengers to trap $O_2^{\bullet-}$ and $^1O_2$, respectively.[1g] For **C-4** alone (Figure 7a,c), an EPR signal was detected in the presence of TEMP (Figure 7c), but not with DMPO (Figure 7a), therefore, $^1O_2$ was produced by **C-4** in aerated solution. With the addition of the sacrificial electron donor, *N*,*N*-diisopropylethylamine, however, an EPR signal was observed only in the presence of DMPO (Figure 7b), no signal being detected with TEMP (Figure 7d), which indicates that only $O_2^{\bullet-}$ was produced in the presence of *N*,*N*-diisopropylethylamine.[1g] These results suggest that the C_{60}–bodipy hybrids can be used as dual functional organic photocatalysts that act as photosensitizers to produce $^1O_2$ (in the photooxidation of dinaphthols) or, with sacrificial electron donors such as *N*,*N*-diisopropylethylamine, $O_2^{\bullet-}$ (aerobic oxidative hydroxylation of arylboronic acids to produce phenols, Scheme 4). To the best of our knowledge, such dual functional organic photocatalysts for photoorganocatalytic reactions have not been reported before.



Scheme 4. Photocatalytic mechanism for the aerobic oxidation of aromatic boronic acids to produce phenols through the generation of the superoxide radical anion ($O_2^{\bullet-}$).

Conclusion

Energy funneling has been used for the first time to prepare heavy-atom-free triplet photosensitizers that show broadband absorption in the visible region. We demonstrated this concept with C_{60}–bodipy triads and tetrads containing two and three light-harvesting antennae with different absorption wavelengths. The panchromatic excitation energy harvested by the antennae in the triads and tetrads was efficiently funneled towards C_{60} (spin converter). Then the triplet excited state was produced by the intrinsic intersystem crossing (ISC) effect of C_{60}. The triplet excited states of the dyads or triads are localized on either the C_{60} unit or the styryl-bodipy units. In the latter case, backward triplet energy transfer occurs from C_{60} to the antenna. Notably, these triplet photosensitizers are heavy-atom-free. They exhibit a broadband absorption, which is in contrast to the narrow visible-light absorption bands of conventional triplet photosensitizers based on a monochromophore profile. Furthermore, these heavy-atom-free triplet photosensitizers possess a predictable ISC effect. The C_{60} triads and tetrads were used as dual functional photocatalysts for two different photocatalytic reactions, namely singlet oxygen ($^1O_2$) mediated photooxidation of naphthol to produce juglone and superoxide radical anion ($O_2^{\bullet-}$) mediated photocatalytic aerobic oxidation of aromatic boronic acids to produce phenols. The new photosensitizers show excellent $^1O_2$ sensitizing properties, a factor of 3.6 greater than the reference compound C_{60}–styryl-bodipy dyad, which contains only one light-harvesting unit. Most importantly, the $^1O_2$ sensitizing ability of the C_{60} triad is a factor of 8.9 greater than conventional organic triplet photosensitizers such as tetraphenylporphyrin (TPP) and methylene blue (MB). Furthermore, the reaction time for the aerobic oxidation of aromatic boronic acids was greatly reduced from 69–96 h for a Ru^{II}–polyimine complex photosensitizer to less than 4 h for the new triplet photosensitizers. The molecular design strategy of these C_{60}–bodipy triads and tetrads, which contain two or three different light-harvesting antennae to ensure a broadband absorption in the visible range, efficient excitation energy funneling to the triplet manifold of the photosensitizers, and the application of these C_{60}–organic chromophore hybrids as dual functional photoorganocatalysts, will be useful for the design of new heavy-atom-free organic triplet photosensitizers. The application of these photosensitizers in areas such as photocatalysis and photodynamic therapy is also promising.

Experimental Section

NMR spectra were recorded on a 400 MHz Varian Unity Inova spectrometer. Mass spectra were recorded with a Q-TOF Micro MS spectrometer. UV/Vis spectra were recorded on an Agilent 8453 UV/Vis spectrophotometer. Fluorescence spectra were recorded on Shimadzu RF5301 PC and Sanco 970 CRT spectrofluorimeters. Luminescence quantum yields were determined by using bodipy ($\Phi_F=72.0\,\%$ in THF) and 2,6-diiodo-bodipy as standards ($\Phi_F=2.7\,\%$ in MeCN). Luminescence lifetimes were measured with an OB920 luminescence lifetime spectrometer (Edinburgh, UK). Typical synthetic methods are presented below. For detailed synthetic procedures of the other compounds, see the Supporting Information.

Compound 2: 4′-Bromophenyl-bodipy (**1**; 120.0 mg, 0.30 mmol) and 4-formylphenylboronic (90.0 mg, 0.6 mmol) were dissolved in toluene/ethanol/water (2:2:1, v/v/v, 25 mL). K_2CO_3 (41.7 mg, 0.3 mmol) was added and argon was bubbled through the solution for 30 min. [Pd(PPh$_3$)$_4$] (0.03 mmol, 18.4 mg) was added. The mixture was heated at reflux under an argon for 8 h. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography (silica gel, dichloromethane (DCM)/petroleum ether, 1:1, v/v) to give a deep-red solid (110.0 mg, 85 %). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 10.09$ (s, 1 H), 8.02 (d, $J = 8.0$ Hz, 2 H), 7.86–7.80 (m, 4 H), 7.43 (d, $J = 7.6$ Hz, 2 H), 6.01 (s, 2 H), 2.57 (s, 6 H), 1.45 ppm (s, 6 H).

Compound 3: Compound **2** (110.0 mg, 0.20 mmol) was dissolved in dry CH_2Cl_2 (50 mL). *N*-Iodosuccinimide (NIS, 44.6 mg, 0.2 mmol) was slowly added. The mixture was stirred at room temp. for 2 h. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography (silica gel, DCM/petroleum ether, 1:1, v/v) to give a deep-red solid (110.0 mg, 61 %). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 10.09$ (s, 1 H), 8.02 (d, $J = 8.0$ Hz, 2 H), 7.86–7.81 (m, 4 H), 7.41 (d, $J = 7.6$ Hz, 2 H), 6.01 (s, 1 H), 2.65 (s, 3 H), 2.58 (s, 3 H), 1.45 ppm (s, 6 H); HRMS (MALDI): *m*/*z* calcd for $[C_{26}H_{22}BOF_2N_2I]^+$: 554.0838; found: 554.0844.

Compound 5: Under argon, **4** (135.2 mg 0.3 mmol) was dissolved in dry DMF (5 mL). Benzaldehyde (142.4 mg, 0.8 mmol) was added, followed by acetic acid (6 drops) and piperidine (6 drops). The mixture was subjected to microwave irradiation (5 min, 150 °C, 1 min pre-stirring). After removal of the solvent under reduced pressure, the crude product was purified by column chromatography (silica gel, DCM) to give deep-purple solid (75.0 mg, 40 %). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.94$ (d, $J = 8.4$ Hz, 2 H), 7.77 (d, $J = 16.4$ Hz, 2 H), 7.65 (d, $J = 8.0$ Hz, 4 H), 7.42–7.39 (m, 4 H), 7.36–7.32 (m, 4 H), 7.28–7.24 (m, 2 H), 6.65 (s, 2 H), 1.44 (s, 6 H), 1.25 ppm (s, 12 H); HRMS (MALDI): *m*/*z* calcd for $[C_{39}H_{38}B_2F_2N_2O_2]^+$: 626.3087; found: 626.3041.

Compound 6: Compounds **3** (45.0 mg 0.1 mmol) and **5** (69.9 mg, 0.11 mmol) were dissolved in dry toluene/ethanol/water (2:2:1, v/v/v, 25 mL). K_2CO_3 (41.6 mg, 0.3 mmol) was added and argon was bubbled through the solution for 30 min. [Pd(PPh$_3$)$_4$] (6.4 mg, 0.005 mmol) was added. The mixture was heated at reflux under argon for 8 h. After removal of the solvent under reduced pressure, the mixture was purified by column chromatography (silica gel, DCM) to give a deep-purple solid (67.6 mg, 72 %). ^{1}H NMR (400 MHz, CDCl3): $\delta = 10.09$ (s, 1 H), 8.02 (d, $J = 8.4$ Hz, 2 H), 7.86 (m, 4 H), 7.76 (d, $J = 16.4$ Hz, 2 H), 7.64 (d, $J = 7.6$ Hz, 4 H), 7.48 (d, $J = 8.8$ Hz, 2 H), 7.42–7.39 (m, 4 H) 7.37–7.34 (m, 4 H), 7.30 (d, $J = 7.2$ Hz, 3 H), 7.24 (s, 1 H), 6.65 (s, 2 H), 6.07 (s, 1 H), 2.62 (s, 3 H), 2.56 (s, 3 H), 1.49 (s, 6 H), 1.47 (s, 3 H), 1.40 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 192.0$, 157.0, 155.9, 153.4, 152.8, 146.1, 145.0, 143.9, 143.1, 142.1, 140.6, 140.4, 138.8, 138.7, 136.7, 136.5, 135.7, 135.5, 135.4, 134.8, 134.1, 133.5, 132.9, 132.1, 131.5, 131.1, 130.6, 129.0, 128.6, 128.1, 127.8, 127.7, 122.1, 121.5, 119.3, 118.1, 30.3, 29.3, 23.5, 23.3, 14.3, 11.3 ppm; HRMS (MALDI): *m*/*z* calcd for $[C_{59}H_{48}B_2OF_4N_4]^+$: 926.3950; found 926.3941.

C-2: Under argon, compound **6** (27.8 mg, 0.03 mmol), C_{60} (36.0 mg, 0.50 mmol), and *N*-methylglycine (44.5 mg, 0.25 mmol) were suspended in dry toluene (20 mL). The mixture was heated at reflux for 12 h. After completion of the reaction, the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/CH_2Cl_2, 1:2, v/v) to give the product as a blue solid (21.6 mg, 66 %). M.p. >250 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.82$ (d, $J = 7.8$ Hz, 2 H), 7.78 (d, $J = 8.0$ Hz, 3 H), 7.72 (s, 1 H), 7.64 (d, $J = 4.0$ Hz, 4 H), 7.43–7.39 (m, 6 H), 7.36–7.32 (m, 4 H) 7.31–7.28 (m, 5 H), 7.24 (s, 1 H), 6.65 (s, 2 H), 6.05 (s, 1 H), 5.04 (d, $J = 8.4$ Hz, 2 H), 4.32 (d, $J = 8.0$ Hz, 1 H), 3.55 (s, 3 H), 2.61 (s, 3 H), 2.55 (s, 3 H), 1.46 (s, 6 H), 1.38 ppm (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 153.0$, 152.7, 147.4, 147.3, 146.2, 146.0, 145.7, 145.4, 145.2, 144.5, 144.3, 143.9, 143.8, 143.6, 143.2, 143.1, 143.0, 142.8, 142.7, 142.4, 142.2, 142.1, 141.9, 141.7, 141.6, 140.3, 139.9, 139.6, 138.7, 138.1, 137.8, 136.3, 136.0, 135.9, 135.7, 135.6, 134.8, 134.4, 133.9, 133.4, 132.7, 132.1, 132.0, 130.9, 130.2, 128.8, 128.6, 128.5, 127.7, 127.6, 127.5, 127.4, 127.3, 119.3, 117.9, 31.9, 30.2, 30.0, 29.7, 29.4, 22.7, 14.8, 14.5, 14.1, 13.3, 13.1 ppm; HRMS (MALDI): *m*/*z* calcd for $[C_{121}H_{53}B_2F_4N_5]^-$: 1673.4423; found: 1673.4562.

Compound 11: Compound **10** (522.0 mg 1.0 mmol) and 4-formylphenylboronic acid (300.0 mg, 2 mmol) was dissolved in dry toluene/ethanol/water (2:2:1, v/v/v, 75 mL). K_2CO_3 (417.9 mg, 3 mmol) was added and argon was bubbled through the solution for 30 min. [Pd(PPh$_3$)$_4$] (182.2 mg, 0.3 mmol) was added. The mixture was heated at reflux under argon for 8 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography (silica gel, DCM/petroleum ether, 2:1, v/v) to give a deep-red solid (425.2 mg, 82 %). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 10.03$ (s, 1 H), 7.91 (d, $J = 8.0$ Hz, 2 H), 7.34 (d, $J = 7.8$ Hz, 2 H), 7.20 (d, $J = 8.4$ Hz, 2 H), 7.02 (d, $J = 8.8$ Hz, 2 H), 6.04 (s, 1 H), 4.03–4.00 (m, 2 H), 2.59 (s, 3 H), 2.53 (s, 3 H), 1.83–1.81 (m, 2 H), 1.53–1.51 (m, 2 H), 1.38 (s, 3 H), 1.47 (s, 3 H), 1.02–0.98 ppm (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 191.9$, 159.9, 157.0, 152.3, 144.6, 142.7, 140.8, 138.7, 134.9, 129.8, 126.8, 122.0, 115.3, 67.9, 31.4, 30.7, 19.3, 14.9, 14.0, 13.4, 13.0 ppm; HRMS (MALDI): *m*/*z* calcd for $[C_{30}H_{31}BF_2N_2O_2]^+$: 500.2447; found 500.2454.

Compound 12: Compound **11** (400.0 mg, 0.8 mmol) and NIS (223.4 mg, 1.0 mmol) were dissolved in DCM (100 mL). The mixture was stirred at room temperature for 2 h. After removal of the solvent under reduced pressure, the mixture was purified by column chromatography (silica gel, DCM/hexanes, 2:1, v/v) to give a deep-red solid (470.0 mg, 95 %). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 10.03$ (s, 1 H), 7.92 (d, $J = 7.6$ Hz, 2 H), 7.34 (d, $J = 8.4$ Hz, 2 H), 7.18 (d, $J = 7.2$ Hz, 2 H), 7.04 (d, $J = 8.0$ Hz, 2 H), 4.03–4.00 (m, 2 H), 2.59 (s, 3 H), 2.53 (s, 3 H), 1.83–1.81 (m, 2 H), 1.53–1.51 (m, 2 H), 1.38 (s, 3 H), 1.47 (s, 3 H), 1.02–0.98 ppm (m, 3 H); HRMS (MALDI): *m*/*z* calcd for $[C_{30}H_{30}BF_2N_2O_2I]^+$: 626.1413; found 626.1469.

Compound 13: Compound **12** (401.6 mg, 0.64 mmol) and **4** (346.5 mg, 0.77 mmol) were dissolved in dry toluene/ethanol/water (2:2:1, v/v/v, 75 mL). K_2CO_3 (417.7 mg, 3 mmol) was added and argon was bubbled through the solution for 30 min. [Pd(PPh$_3$)$_4$] (76.8 mg, 0.064 mmol) was added. The mixture was heated at reflux under argon for 8 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography (silica gel, DCM/hexanes, 2:1, v/v) to give a deep-red solid (450.0 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 10.04$ (s, 1 H), 7.93 (d, $J = 7.6$ Hz, 2 H), 7.37–7.30 (m, 6 H), 7.25–7.23 (m, 2 H), 7.04 (d, $J = 8.8$ Hz, 2 H), 6.00 (s, 2 H), 4.03–4.00 (m, 2 H), 2.56 (s, 12 H), 1.80–1.79 (m, 2 H), 1.41 (s, 12 H), 1.02–0.98 ppm (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 192.0$, 160.1, 155.7, 143.2, 140.6, 140.0, 139.5, 135.1, 134.6, 133.4, 132.4, 132.0, 131.8, 131.6, 131.3, 131.1, 130.9, 129.9, 129.2, 128.2, 121.5, 115.5, 63.1, 31.4, 19.4, 14.8, 14.4, 14.1, 13.7, 13.6, 13.4, 13.3 ppm; HRMS (MALDI): *m*/*z* calcd for $[C_{49}H_{48}B_2F_4N_4O_2]^+$: 822.3900; found: 822.3848.

C-4: Under argon, compound **13** (24.7 mg, 0.03 mmol), C_{60} (42.0 mg, 0.06 mmol), and *N*-methylglycine (17.8 mg, 0.20 mmol) were suspended in dry toluene (50 mL). The mixture was heated at reflux for 12 h. After completion of the reaction, the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, petroleum ether/CH_2Cl_2, 1:2, v/v) to give the product as a red solid (32.4 mg, 66 %). M.p. >250 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.73$–7.70 (m, 1 H), 7.55–7.52 (m, 1 H), 7.32–7.29 (m, 5 H), 7.23–6.19 (m, 3 H), 7.01 (d, $J = 7.6$ Hz, 2 H), 5.99 (s, 2 H), 5.30 (s, 1 H), 4.00–3.97 (m, 2 H), 2.56–2.51 (m, 12 H), 2.36 (s, 3 H), 2.34 (s, 2 H), 1.84–1.80 (m, 2 H), 1.56–1.52 (m, 2 H), 1.48 (s, 3 H), 1.45 (s, 3 H), 1.38 (s, 6 H), 0.98–0.96 ppm (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 159.9$, 155.6, 147.5, 147.4, 146.3, 146.3, 146.2, 146.0, 145.8, 145.7, 145.6, 145.5, 145.4, 145.3, 145.2, 145.1, 145.0, 144.9, 144.8, 144.7, 144.6, 144.5, 144.4, 144.2, 144.1, 143.2, 143.0, 142.6, 142.5, 142.1, 142.0, 141.9, 141.7, 141.4, 140.2, 140.1, 139.8, 139.7, 139.3, 139.1, 137.9, 135.8, 134.7, 133.8, 132.7, 131.8, 131.4, 131.0, 129.0, 128.0, 127.0, 125.3, 121.3, 115.2, 67.9, 40.2, 29.7, 19.2, 14.6, 14.2, 13.9, 13.5, 13.2, 13.1 ppm; HRMS (MALDI): *m*/*z* calcd for $[C_{111}H_{53}B_2F_4N_5O_1]^-$: 1569.4372; found: 1569.4390.

Photooxidation: The photooxidation experiments were carried out as follows.[41] A CH_2Cl_2/MeOH (9:1, v/v) mixed solvent containing DHN (2.0×10^{-4} M) and a triplet photosensitizer (5 mol % with respect to DHN) was placed in a two-neck round-bottomed flask (25 mL). The solution was then irradiated by using a 35 W xenon lamp (with focusing reflector) and a cut-off filter (0.72 M $NaNO_2$ aqueous solution, which is transparent for light with wavelength >385 nm). UV/Vis absorption spectra were recorded at intervals of 2–5 min. The DHN consumption was monitored by following the decrease in the UV absorption at 301 nm, and the concentration of DHN was calculated based on its molar absorption coefficient ($\varepsilon = 7664\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$). On the other hand, the production of juglone was monitored by following the increase in the absorption at 427 nm. The concentration of juglone was calculated from its molar extinction coefficient ($\varepsilon = 3811\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$ at 427 nm) and the its yield was determined by dividing the concentration of juglone by the initial concentration of DHN. The photostability experiments were carried out using the same method but without the substrate DHN.

Measurement of the singlet oxygen quantum yield (Φ_Δ): The Φ_Δ quantum yields were calculated by using methylene blue (MB) in dichloromethane with $\Phi_\Delta = 0.57$ as reference. The absorbance of the $^1O_2$ scavenger, 1,4-diphenylisobenzofuran (DPBF), was adjusted to around 1.0 in air-saturated dichloromethane. Then the photosensitizer was added and its absorbance was adjusted to around 0.2–0.3. Then the cuvette was exposed to monochromatic light at the peak absorption wavelength for 10 s. The absorbance at 630 nm was measured several times after each irradiation. The slope of the absorbance maxima of DPBF at 414 nm versus time graph was calculated for each photosensitizer. The singlet oxygen quantum yields (Φ_Δ) were calculated according to equation (1)

$$\Phi_{\mathrm{sam}} = \Phi_{\mathrm{ref}} \frac{k_{\mathrm{sam}}}{k_{\mathrm{ref}}} \frac{F_{\mathrm{ref}}}{F_{\mathrm{sam}}} \tag{1}$$

in which sam and ref designate "**C-1**, **C-2**" and "MB" respectively, k is the slope of the difference in the change in the absorbance of DPBF (414 nm) with irradiation time, and F is the absorption correction factor, which is given by $F = 1\text{–}10^{-\mathrm{OD}}$ (OD at the irradiation wavelength).

C_{60}–bodipy hybrids as photocatalyst for the aerobic oxidation of aromatic boronic acids to produce phenols: The visible-light-induced aerobic oxidative hydroxylation reactions of arylboronic acids were carried out as follows. A CH_2Cl_2/CH_3CN (5:1, v/v) mixed solvent containing arylboronic acid derivatives (0.1 mmol), triplet photosensitizer (2 mol%), and *N*,*N*-diisopropylethylamine (1.0 mmol, 10 equiv) were placed in a flask (25 mL), The solution was then irradiated by using a 35 W xenon lamp (with focusing reflector) and a cut-off filter (0.72 M $NaNO_2$ aqueous solution, which is transparent for light with a wavelength >385 nm). The reaction was monitored by TLC. After completion of the reaction, the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, methanol/CH_2Cl_2, 1:50, v/v) to give the product as a white solid.

Electron paramagnetic resonance (EPR) spectroscopy: EPR spectra were recorded by using a Bruker ESP-300E spectrometer at 9.8 GHz X-band with 100 Hz field modulation. Samples were quantitatively injected into especially made quartz capillaries for EPR analysis in the dark and illuminated directly in the cavity of the EPR spectrometer. The triplet photosensitizers and superoxide radical anion ($O_2^{\cdot-}$) scavenger 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO), the singlet oxygen ($^1O_2$) scavenger 2,2,6,6-tetramethylpiperidine (TEMP) in air-saturated CH_2Cl_2 was stirred in the dark. Then the solution was injected into the quartz capillary. The photoirradiation was performed by using a diode-pumped solid-state (DPSS) laser (532 nm).

Acknowledgements

We thank the NSFC (20972024, 21073028 and 21273028), the Royal Society (UK), the NSFC (China-UK Cost-Share Science Networks, 21011130154), the Science Foundation Ireland (SFI E.T.S. Walton Program 11/W.1/E2061), the Fundamental Research Funds for the Central Universities (DUT10ZD212), the Ministry of Education (NCET-08-0077 and SRFDP-20120041130005) and the Dalian University of Technology for financial support.

---

[1] a) F. Gärtner, S. Denurra, S. Losse, A. Neubauer, A. Boddien, A. Gopinathan, A. Spannenberg, H. Junge, S. Lochbrunner, M. Blug, S. Hoch, J. Busse, S. Gladiali, M. Beller, *Chem. Eur. J.* **2012**, *18*, 3220–3225; b) Y.-Q. Zou, J.-R. Chen, X.-P. Liu, L.-Q. Lu, R. L. Davis, K. A. Jørgensen, W.-J. Xiao, *Angew. Chem.* **2012**, *124*, 808–812; *Angew. Chem. Int. Ed.* **2012**, *51*, 784–788; c) Y.-Q. Zou, L.-Q. Lu, L. Fu, N.-J. Chang, J. Rong, J.-R. Chen, W.-J. Xiao, *Angew. Chem.* **2011**, *123*, 7309–7313; *Angew. Chem. Int. Ed.* **2011**, *50*, 7171–7175; d) M. Neumann, S. Füldner, B. König, K. Zeitler, *Angew. Chem.* **2011**, *123*, 981–985; *Angew. Chem. Int. Ed.* **2011**, *50*, 951–954; e) S. Maity, M. Zhu, R. S. Shinabery, N. Zheng, *Angew. Chem.* **2012**, *124*, 226–230; *Angew. Chem. Int. Ed.* **2012**, *51*, 222–226; f) M. Cherevatskaya, M. Neumann, S. Füldner, C. Harlander, S. Kümmel, S. Dankesreiter, A. Pfitzner, K. Zeitler, B. König, *Angew. Chem.* **2012**, *124*, 4138–4142; *Angew. Chem. Int. Ed.* **2012**, *51*, 4062–4066; g) Q. Liu, Y.-N. Li, H.-H. Zhang, B. Chen, C.-H. Tung, L.-Z. Wu, *Chem. Eur. J.* **2012**, *18*, 620–627; h) J. Xuan, W.-J. Xiao, *Angew. Chem.* **2012**, *124*, 6934–6944; *Angew. Chem. Int. Ed.* **2012**, *51*, 6828–6838; i) D. Ravelli, M. Fagnoni, A. Albini, *Chem. Soc. Rev.* **2013**, *42*, 97–113; j) S. Fukuzumi, K. Ohkubo, *Chem. Sci.* **2013**, *4*, 561–574.

[2] a) J. I. Goldsmith, W. R. Hudson, M. S. Lowry, T. H. Anderson, S. Bernhard, *J. Am. Chem. Soc.* **2005**, *127*, 7502–7510; b) J. W. Tucker, C. R. J. Stephenson, *J. Org. Chem.* **2012**, *77*, 1617–1622; c) J. D. Nguyen, E. M. D'Amato, J. M. R. Narayanam, C. R. J. Stephenson, *Nat. Chem.* **2012**, *4*, 854–859; d) L. Shi, W. Xia, *Chem. Soc. Rev.* **2012**, *41*, 7687–7697; e) G. Zhao, C. Yang, L. Guo, H. Sun, R. Lin, W. Xia, *J. Org. Chem.* **2012**, *77*, 6302–6306; f) X. Lang, W. Ma, Y. Zhao, C. Chen, H. Ji, J. Zhao, *Chem. Eur. J.* **2012**, *18*, 2624–2631; g) M. Rueping, R. M. Koenigs, K. Poscharny, D. C. Fabry, D. Leonori, C. Vila, *Chem. Eur. J.* **2012**, *18*, 5170–5174; h) J. Lalevée, M. Peter, F. Dumur, D. Gigmes, N. Blanchard, M.-A. Tehfe, F. Morlet-Savary, J. P. Fouassier, *Chem. Eur. J.* **2011**, *17*, 15027–15031; i) L. Huang, J. Zhao, *Chem. Commun.* **2013**, *49*, 3751–3753.

[3] Y. Y. Cheng, B. Fückel, R. W. MacQueen, T. Khoury, R. G. C. R. Clady, T. F. Schulze, N. J. Ekins-Daukes, M. J. Crossley, B. Stannowski, K. Lips, T. W. Schmidt, *Energy Environ. Sci.* **2012**, *5*, 6953–6959.

[4] T. Yogo, Y. Urano, Y. Ishitsuka, F. Maniwa, T. Nagano, *J. Am. Chem. Soc.* **2005**, *127*, 12162–12163.

[5] a) N. Adarsh, R. R. Avirah, D. Ramaiah, *Org. Lett.* **2010**, *12*, 5720–5723; b) N. Adarsh, M. Shanmugasundaram, R. R. Avirah, D. Ramaiah, *Chem. Eur. J.* **2012**, *18*, 12655–12662.

[6] S. G. Awuah, J. Polreis, V. Biradar, Y. You, *Org. Lett.* **2011**, *13*, 3884–3887.

[7] F. Yukruk, A. L. Dogan, H. Canpinar, D. Guc, E. U. Akkaya, *Org. Lett.* **2005**, *7*, 2885–2887.

[8] a) Y. Cakmak, S. Kolemen, S. Duman, Y. Dede, Y. Dolen, B. Kilic, Z. Kostereli, L. T. Yildirim, A. L. Dogan, D. Guc, E. U. Akkaya, *Angew. Chem.* **2011**, *123*, 12143–12147; *Angew. Chem. Int. Ed.* **2011**, *50*, 11937–11941; b) B. Ventura, G. Marconi, M. Bröring, R. Krüger, L. Flamigni, *New J. Chem.* **2009**, *33*, 428–438; c) Y. Wu, Y. Zhen, Y. Ma, R. Zheng, Z. Wang, H. Fu, *J. Phys. Chem. Lett.* **2010**, *1*, 2499–2502.

[9] a) R. Gao, D. G. Ho, B. Hernandez, M. Selke, D. Murphy, P. I. Djurovich, M. E. Thompson, *J. Am. Chem. Soc.* **2002**, *124*, 14828–14829; b) F. Schmitt, J. Freudenreich, N. P. E. Barry, L. J. Jeanneret, G. Süss-Fink, B. Therrien, *J. Am. Chem. Soc.* **2012**, *134*, 754–757; c) A. E. O'Connor, W. M. Gallagher, A. T. Byrne, *Photochem. Photobiol.* **2009**, *85*, 1053–1074; d) A. Kamkaew, S. H. Lim, H. B. Lee, L. V. Kiew, L. Y. Chung, K. Burgess, *Chem. Soc. Rev.* **2013**, *42*, 77–88; e) S. G. Awuahab, Y. You, *RSC Adv.* **2012**, *2*, 11169–11183; f) J. Zhao, W. Wu, J. Sun, S. Guo, *Chem. Soc. Rev.* **2013**, *42*, 5323–5351.

[10] a) A. Gorman, J. Killoran, C. O'Shea, T. Kenna, W. M. Gallagher, D. F. O'Shea, *J. Am. Chem. Soc.* **2004**, *126*, 10619–10631; b) S. O. McDonnell, M. J. Hall, L. T. Allen, A. Byrne, W. M. Gallagher, D. F. O'Shea, *J. Am. Chem. Soc.* **2005**, *127*, 16360–16361; c) D. O. Frimannsson, M. Grossi, J. Murtagh, F. Paradisi, D. F. O'Shea, *J. Med. Chem.* **2010**, *53*, 7337–7343; d) P. Batat, M. Cantuel, G. Jonusauskas, L. Scarpantonio, A. Palma, D. F. O'Shea, N. D. McClenaghan, *J. Phys. Chem. A* **2011**, *115*, 14034–14039.

[11] T. N. Singh-Rachford, F. N. Castellano, *Coord. Chem. Rev.* **2010**, *254*, 2560–2573.

[12] A. Monguzzi, J. Mezyk, F. Scotognella, R. Tubino, F. Meinar, *Phys. Rev. B* **2008**, *78*, 195112.

[13] a) S. Baluschev, T. Miteva, V. Yakutkin, G. Nelles, A. Yasuda, G. Wegner, *Phys. Rev. Lett.* **2006**, *97*, 143903; b) Y. Y. Cheng, T. Khoury, R. G. C. R. Clady, M. J. Y. Tayebjee, N. J. Ekins-Daukes, M. J. Crossley, T. W. Schmidt, *Phys. Chem. Chem. Phys.* **2010**, *12*, 66–71.

[14] a) J. Zhao, S. Ji, H, Guo, *RSC Adv.* **2011**, *1*, 937–950; b) J. Zhao, S. Ji, W. Wu, W. Wu, H. Guo, J. Sun, H. Sun, Y. Liu, Q. Li, L. Huang, *RSC Adv.* **2012**, *2*, 1712–1728.

[15] P. Ceroni, *Chem. Eur. J.* **2011**, *17*, 9560–9564.

[16] N. J. Turro, V. Ramamurthy, J. C. Scaiano, *Principles of Molecular Photochemistry: An Introduction*, University Science Books, Sausalito, **2009**.

[17] H. C. Chen, C. Y. Hung, K. H. Wang, H. L. Chen, W. S. Fann, F. C. Chien, P. Chen, T. J. Chow, C. P. Hsu, S. S. Sun, *Chem. Commun.* **2009**, 4064–4066.

[18] a) O. A. Bozdemir, S. E. Cakmak, O. O. Ekiz, A. Dana, E. U. Akkaya, *Angew. Chem.* **2011**, *123*, 11099–11104; *Angew. Chem. Int. Ed.* **2011**, *50*, 10907–10912; b) Z. Kostereli, T. Ozdemir, O. Buyukcakir, E. U. Akkaya, *Org. Lett.* **2012**, *14*, 3636–3639; c) W. Lin, L. Yuan, Z. Cao, Y. Feng, J. Song, *Angew. Chem.* **2010**, *122*, 385–389; *Angew. Chem. Int. Ed.* **2010**, *49*, 375–379; d) J. Han, J. Jose, E. Mei, K. Burgess, *Angew. Chem.* **2007**, *119*, 1714–1717; *Angew. Chem. Int. Ed.* **2007**, *46*, 1684–1687; e) B. Du, P. D. Harvey, *Chem. Commun.* **2012**, *48*, 2671–2673; f) S. Kömürlü, S. H. Lee, T. McCarley, K. S. Schanze, V. D. Kleiman, *J. Phys. Chem. B* **2011**, *115*, 15214–15220.

[19] a) R. Ziessel, A. Harriman, *Chem. Commun.* **2011**, *47*, 611–631; b) X. Zhang, Y. Xiao, X. Qian, *Org. Lett.* **2008**, *10*, 29–32; c) J.-Y. Liu, Y. Huang, R. Menting, B. Röder, E. A. Ermilov, D. K. P. Ng, *Chem. Commun.* **2013**, *49*, 2998–3000; d) M. E. El-Khouly, A. N. Amin, M. E. Zandler, S. Fukuzumi, F. D′Souza, *Chem. Eur. J.* **2012**, *18*, 5239–5247; e) T. Bura, F. Nastasi, F. Puntoriero, S. Campagna, R. Ziessel, *Chem. Eur. J.* **2013**, *19*, 8900–8912.

[20] a) J. Qu, N. G. Pschirer, D. Liu, A. Stefan, F. C. De Schryver, K. Müllen, *Chem. Eur. J.* **2004**, *10*, 528–537; b) E. Fron, L. Puhl, I. Oesterling, C. Li, K. Müllen, F. C. De Schryver, J. Hofkens, T. Vosch, *ChemPhysChem* **2011**, *12*, 595–608.

[21] a) M. A. Oar, J. M. Serin, W. R. Dichtel, J. M. J. Fréchet, T. Y. Ohulchanskyy, P. N. Prasad, *Chem. Mater.* **2005**, *17*, 2267–2275; b) M. A. Oar, W. R. Dichtel, J. M. Serin, J. M. J. Fréchet, J. E. Rogers, J. E. Slagle, P. A. Fleitz, L.-S. Tan, T. Y. Ohulchanskyy, P. N. Prasad, *Chem. Mater.* **2006**, *18*, 3682–3692; c) C.-Y. Chen, Y. Tian, Y.-J. Cheng, A. C. Young, J.-W. Ka, A. K.-Y. Jen, *J. Am. Chem. Soc.* **2007**, *129*, 7220–7221.

[22] J. W. Arbogast, A. P. Darmanyan, C. S. Foote, Y. Rubin, F. N. Diederich, M. M. Alvarez, S. J. Anz, R. L. Whetten, *J. Phys. Chem.* **1991**, *95*, 11–12.

[23] Y. Rio, W. Seitz, A. Gouloumis, P. Vázquez, J. L. Sessler, D. M. Guldi, T. Torres, *Chem. Eur. J.* **2010**, *16*, 1929–1940.

[24] D. González-Rodríguez, T. Torres, M. Á. Herranz, L. Echegoyen, E. Carbonell, D. M. Guldi, *Chem. Eur. J.* **2008**, *14*, 7670–7679.

[25] R. F. Enes, J.-J. Cid, A. Hausmann, O. Trukhina, A. Gouloumis, P. Vàzquez, J. A. S. Cavaleiro, A. C. Tomé, D. M. Guldi, T. Torres, *Chem. Eur. J.* **2012**, *18*, 1727–1736.

[26] a) M. Ince, A. Hausmann, M. V. Martínez-Díaz, D. M. Guldi, T. Torres, *Chem. Commun.* **2012**, *48*, 4058–4060; b) V. Bandi, M. E. El-Khouly, K. Ohkubo, V. N. Nesterov, M. E. Zandler, S. Fukuzumi, F. D′Souza, *Chem. Eur. J.* **2013**, *19*, 7221–7230.

[27] a) D. González-Rodríguez, E. Carbonell, D. M. Guldi, T. Torres, *Angew. Chem.* **2009**, *121*, 8176–8180; *Angew. Chem. Int. Ed.* **2009**, *48*, 8032–8036; b) J.-F. Nierengarten, *New J. Chem.* **2004**, *28*, 1177–1191; c) J.-F. Nierengarten, J.-F. Eckert, J.-F. Nicoud, L. Ouali, V. Krasnikov, G. Hadziioannou, *Chem. Commun.* **1999**, 617–618; d) F. D′Souza, A. N. Amin, M. E. El-Khouly, N. K. Subbaiyan, M. E. Zandler, S. Fukuzumi, *J. Am. Chem. Soc.* **2012**, *134*, 654–664; e) A. M. V. M. Pereira, A. Hausmann, J. P. C. Tomé, O. Trukhina, M. Urbani, M. G. P. M. S. Neves, J. A. S. Cavaleiro, D. M. Guldi, T. Torres, *Chem. Eur. J.* **2012**, *18*, 3210–3219; f) T. W. Chamberlain, E. S. Davies, A. N. Khlobystov, N. R. Champness, *Chem. Eur. J.* **2011**, *17*, 3759–3767.

[28] a) A. N. Amin, M. E. El-Khouly, N. K. Subbaiyan, M. E. Zandler, S. Fukuzumi, F. D′Souza, *Chem. Commun.* **2012**, *48*, 206–208; b) H. Imahori, T. Umeyama, K. Kurotobi, Y. Takano, *Chem. Commun.* **2012**, *48*, 4032–4045; c) W. Wu, J. Zhao, J. Sun, S. Guo, *J. Org. Chem.* **2012**, *77*, 5305–5312.

[29] a) N. Armaroli, G. Accorsi, D. Felder, J.-F. Nierengarten, *Chem. Eur. J.* **2002**, *8*, 2314–2323; b) G. Accorsi, N. Armaroli, *J. Phys. Chem. C* **2010**, *114*, 1385–1403; c) D. Bonifazi, M. Scholl, F. Song, L. Echegoyen, G. Accorsi, N. Armaroli, F. Diederich, *Angew. Chem.* **2003**, *115*, 5116–5120; *Angew. Chem. Int. Ed.* **2003**, *42*, 4966–4970; d) D. M. Lyons, J. Mohanraj, G. Accorsi, N. Armaroli, P. D. W. Boyd, *New J. Chem.* **2011**, *35*, 632–639; e) L. Y. Chiang, P. A. Padmawar, J. E. Rogers-Haley, G. So, T. Canteenwala, S. Thota, L.-S. Tan, K. Pritzker, Y.-Y. Huang, S. K. Sharma, D. B. Kurup, M. R. Hamblin, B. Wilsone, A. Urbasb, *J. Mater. Chem.* **2010**, *20*, 5280–5293; f) F. Prat, C. Martí, S. Nonell, X. Zhang, C. S. Foote, R. G. Moreno, J. L. Bourdelandec, J. Font, *Phys. Chem. Chem. Phys.* **2001**, *3*, 1638–1643; g) Y. Iwamoto, Y. Yamakoshi, *Chem. Commun.* **2006**, 4805–4807; h) T. M. Figueira-Duarte, A. Gégout, J.-F. Nierengarten, *Chem. Commun.* **2007**, 109–119; i) Y. Matsuo, T. Ichiki, E. Nakamura, *J. Am. Chem. Soc.* **2011**, *133*, 9932–9937.

[30] a) J. Y. Liu, M. E. El-Khouly, S. Fukuzumi, D. K. P. Ng, *Chem. Asian J.* **2011**, *6*, 174–179; b) M. Urbani, K. Ohkubo, D. M. S. Islam, S. Fukuzumi, F. Langa, *Chem. Eur. J.* **2012**, *18*, 7473–7485.

[31] R. Ziessel, B. D. Allen, D. B. Rewinska, A. Harriman, *Chem. Eur. J.* **2009**, *15*, 7382–7393.

[32] a) A. Loudet, K. Burgess, *Chem. Rev.* **2007**, *107*, 4891–4932; b) G. Ulrich, R. Ziessel, A. Harriman, *Angew. Chem.* **2008**, *120*, 1202–1219; *Angew. Chem. Int. Ed.* **2008**, *47*, 1184–1201.

[33] a) J.-S. Lu, H. Fu, Y. Zhang, Z. J. Jakubek, Y. Tao, S. Wang, *Angew. Chem.* **2011**, *123*, 11862–11866; *Angew. Chem. Int. Ed.* **2011**, *50*, 11658–11662; b) Y.-W. Wang, A. B. Descalzo, Z. Shen, X.-Z. You, K. Rurack, *Chem. Eur. J.* **2012**, *18*, 7306–7309; c) J.-Y. Liu, M. E. El-Khouly, S. Fukuzumi, D. K. P. Ng, *ChemPhysChem* **2012**, *13*, 2030–2036; d) S.-L. Niu, C. Massif, G. Ulrich, P.-Y. Renard, A. Romieu, R Ziessel, *Chem. Eur. J.* **2012**, *18*, 7229–7242; e) D. Wang, J. Fan, X. Gao, B. Wang, S. Sun, X. Peng, *J. Org. Chem.* **2009**, *74*, 7675–7683; f) X. Qu, Q. Liu, X. Ji, H. Chen, Z. Zhou, Z. Shen, *Chem. Commun.* **2012**, *48*, 4600–4602; g) X.-D. Jiang, J. Zhang, T. Furuyama, W. Zhao, *Org. Lett.* **2012**, *14*, 248–251.

[34] a) C. C. Hofmann, S. M. Lindner, M. Ruppert, A. Hirsch, S. A. Haque, M. Thelakkat, J. Köhler, *J. Phys. Chem. B* **2010**, *114*, 9148–9156; b) C. C. Hofmann, S. M. Lindner, M. Ruppert, A. Hirsch, S. A. Haque, M. Thelakkat, J. Köhler, *Phys. Chem. Chem. Phys.* **2010**, *12*, 14485–14491.

[35] A. Lembo, P. Tagliatesta, D. M. Guldi, M. Wielopolski, M. Nuccetelli, *J. Phys. Chem. A* **2009**, *113*, 1779–1793.

[36] J. Baffreau, L. Ordronneau, S. Leroy-Lhez, P. Hudhomme, *J. Org. Chem.* **2008**, *73*, 6142–6147.

[37] J. Y. Liu, M. E. El-Khouly, S. Fukuzumi, D. K. P. Ng, *Chem. Eur. J.* **2011**, *17*, 1605–1613.

[38] a) Y. Liu, J. Zhao, *Chem. Commun.* **2012**, *48*, 3751–3753; b) L. Huang, X. Yu, W. Wu, J. Zhao, *Org. Lett.* **2012**, *14*, 2594–2597.

[39] M. Baruah, W. Qin, C. Flors, J. Hofkens, R. A. L. Vallée, D. Beljonne, M. V. Auweraer, W. M. D. Borggraeve, N. Boens, *J. Phys. Chem. A* **2006**, *110*, 5998–6009.

[40] Y. Chen, J. Zhao, H. Guo, L. Xie, *J. Org. Chem.* **2012**, *77*, 2192–2206.

[41] S. Takizawa, R. Aboshi, S. Murata, *Photochem. Photobiol. Sci.* **2011**, *10*, 895–903.

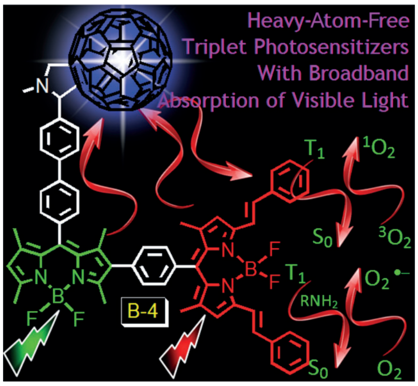
[42] J. Sun, J. Zhao, H. Guo, W. Wu, *Chem. Commun.* **2012**, *48*, 4169–4171.

Received: June 27, 2013

Photochemistry

*L. Huang, X. Cui, B. Therrien, J. Zhao** …………………… ■■■■–■■■■

Energy-Funneling-Based Broadband Visible-Light-Absorbing Bodipy–C_{60} Triads and Tetrads as Dual Functional Heavy-Atom-Free Organic Triplet Photosensitizers for Photocatalytic Organic Reactions



Fullerene photocatalysts: Broadband visible-light-absorbing, heavy-atom-free triplet photosensitizers based on bodipy–C_{60} dyads, triads, and tetrads have been prepared (see figure). Resonance energy transfer or intramolecular funneling was used to achieve panchromatic absorption in the visible region. The triplet photosensitizers were used as dual functional photoorganocatalysts to produce $^1O_2$ or $O_2^{\bullet-}$. The $^1O_2$ sensitizing ability of the new photosensitizers is up to a factor of 8.9 greater than other known triplet photosensitizers based on a monochromophore such as methylene blue.