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Styryl Bodipy-C_{60} Dyads as Efficient Heavy-Atom-Free Organic Triplet Photosensitizers

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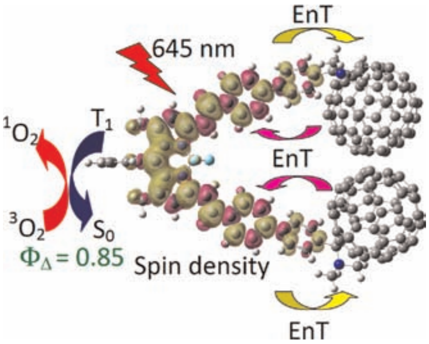
ABSTRACT



C_{60}-styryl Bodipy dyads that show strong absorption of visible light ($\varepsilon = 64\,600$ M^{-1} cm^{-1} at 657 nm) and a long-lived triplet excited state ($\tau_T = 123.2$ μs) are prepared. The dyads were used as heavy-atom-free organic triplet photosensitizers for photooxidation of 1,5-dihydroxynaphthalene via the photosensitizing of singlet oxygen ($^1O_2$). The photooxidation efficiency of the dyads compared to the conventional Ir(III) complex $^1O_2$ photosensitizer increased 19-fold.

Triplet photosensitizers have attracted much attention, due to their applications in photocatalysis,[1] photovoltaics,[2] photodynamic therapy (PDT),[3,4] photopolymerization,[5] luminescent molecular probes,[6,7] and more recently the triplet–triplet annihilation photon upconversions.[8,9] Traditionally the triplet photosensitizers are transition metal complexes, such as the Pt(II), Ir(III), Ru(II) complexes.[10–13] The heavy atom effect facilitates intersystem crossing (ISC), thus the triplet excited states of the complexes can be populated upon photoexcitation. However, these complexes are expensive and most molecular structures cannot be as readily derivatized as an organic chromophore.[11,12] Another kind of triplet sensitizer is the iodo- or bromo-containing organic chromophores.[4,14–16] A third kind of triplet photosensitizer is without any heavy atoms, such as

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2,3-butanedione, benzophenone, porphyrins, etc. Unfortunately, the absorption of these compounds is usually in the UV range (except porphyrins). Furthermore, the ISC property is *unpredictable* for the *derivatives* of these compounds; e. g. the ISC property will disappear with derivatization. It is still a substantial challenge to design a heavy-atom-free *organic* triplet photosensitizer showing the *predetermined* ISC property.[18,19]

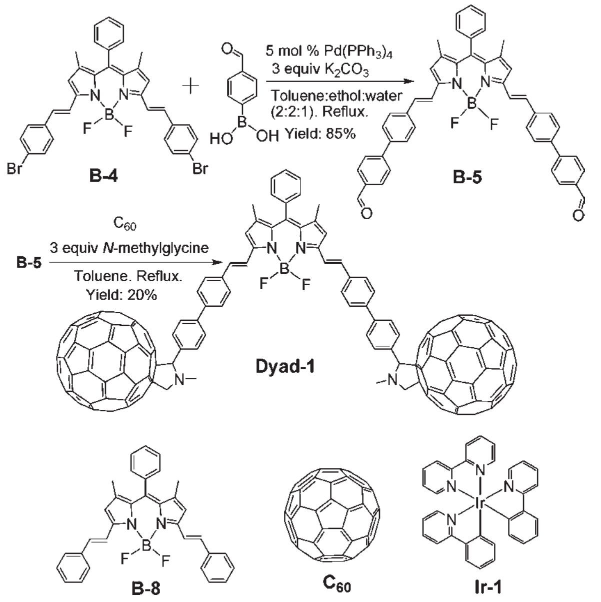
In regards to this aspect, the efficient ISC of fullerene C_{60} is particularly interesting.[17,20] However, C_{60} itself is not an ideal triplet photosensitizer because its absorption in the visible range is extremely weak. C_{60} does show an absorption band at ca. 700 nm. This weak, yet crucial absorption, indicating the presence of a low-lying sinlget excited state, guarantees intramolecular energy transfer (EnT) in C_{60}-organic chromophore dyads.[21−28] C_{60}-organic chromophore dyads have been reported; however, to the best of our knowledge, the C_{60} dyads have not been used for sensitizing a photophysical process, such as the production of singlet oxygen ($^1O_2$).[29]

Herein we devised visible light-harvesiting C_{60} dyads (**Dyad-1**−**3**, Scheme 1 and Figure 1). Styryl-Bodipys were used as the light harvesting antennas, and C_{60} units act as the *spin convertor*. The dyads show strong absorption of visible light and very long-lived triplet excited states. **Dyad-1**−**3** are used as efficient triplet photosensitizers for the photooxidation of DHN, via sensitizing of singlet oxygen ($^1O_2$).[30] The performance of these dyads is much better than the conventional $^1O_2$ photosensitizers (see later section).

Light harvesting antenna styryl-Bodipys were usually obtained in low yields via the Knoevenagel condensation (usually < 30%).[27] Herein we developed an efficient preparation protocol by using microwave irradiation and high boiling point solvents. The intermediate **B-4** was obtained in 93% yield (Supporting Information (SI)). Suzuki cross-coupling between **B-4** and 4-formylbenzeneboronic acid affords **B-5**. A Prato reaction between **B-5**, C_{60}, and *N*-methylglycine gave **Dyad-1**. A similar method was used for the preparation of **Dyad-2** and **Dyad-3** (Figure 1 and SI). The solubility of **Dyad-3** is poor in normal organic solvents, and only elemental analysis can be performed.

The design rationale of **Dyad-1**−**3** lies in the notion that antenna **B-8** shows strong absorption in the visible range.[31] Its S_1 state energy level (1.93 eV) is higher than the S_1 state of C_{60} (1.72 eV); thus intramolecular EnT from the Bodipy to C_{60} unit will occur.[27] With population of the S_1 state of C_{60}, the triplet state of C_{60} will be populated via the intrinsic ISC of C_{60}. However, the T_1 states of the dyads do not necessarily localize on the C_{60} unit. The localization of the T_1 state is dependent on the energy level of the light-harvesting antenna and the C_{60} unit. A "ping-pong" energy transfer may occur;[26a,32,33] that is, first the energy transfer from the antenna to the C_{60} unit (can be also considered as

Scheme 1. Synthesis of the Styryl-Bodipy Dyad **Dyad-1**



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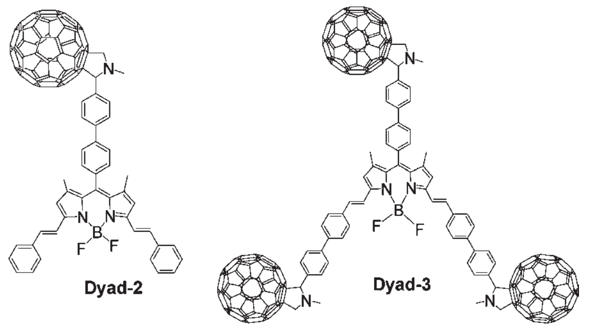

Figure 1. Molecular structure of **Dyad-2** and **Dyad-3** (please refer to the SI for synthetic details).

internal conversion, IC) and in turn the backward triplet state EnT from C_{60} to the Bodipy antenna will occur, if the T_1 state energy level of the antenna is lower than that of C_{60}.[26a,27a,33]

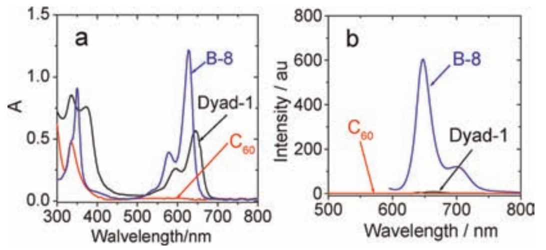

Figure 2. (a) UV–vis absorption and (b) fluorescence emission spectra of **Dyad-1**, **B-8**, and C_{60}. Excited at 620, 590, and 320 nm, respectively. In toluene (1.0×10^{-5} M; 20 °C).

The absorptions of the antenna and **Dyad-1** were compared (Figure 2a). C_{60} absorbs very weakly in the visible range, with the maximum at 335 nm. Conversely, the light-harvesting antenna **B-8** gives strong absorption at 629 nm (ε = 120000 M^{-1} cm^{-1}). **Dyad-1** absorbs at 645 nm (ε = 56800 M^{-1} cm^{-1}). Similar absorption was found for **Dyad-2** and **-3** (see SI). We noted that the UV absorption of the C_{60} unit in the dyads is not proportional to the number of C_{60} units in the dyads; a phenomenon was also found for C_{60}-containing dendrimers.[34]

C_{60} shows weak fluorescence ($\Phi_F < 0.1\%$) (Figure 2b). Conversely, **B-8** gives intense fluorescence at 641 nm (Φ_F = 59%). Interestingly, **Dyad-1** fluoresces weakly (Φ_F = 1.0%). The quenched fluorescence of the antenna in **Dyad-1** is due to the intramolecular singlet state energy transfer from the antenna to the C_{60} unit.[26] We demonstrated that the quenching is not due to the electron transfer from the N-atom in the pyrrolidine rings, studied by protonation with trifluoroacetic acid (see SI). The energy transfer efficiency is calculated as 98.1%.[26] A similar emission property was found for **Dyad-2** and **Dyad-3** (see SI). These results indicate that *one* C_{60} unit in the dyad is sufficient to quench the emission of the antenna; i.e. efficient intramolecular EnT is imparted.

In order to confirm the production of the T_1 state of **Dyad-1** upon photoexcitation, nanosecond time-resolved transient absorption was studied (Figure 3). Upon pulsed laser excitation at 532 nm, bleaching at 645 and 370 nm was observed, which coincides with the steady-state absorption of antenna **B-8** (Figure 2a). Thus the bleaching can be attributed to depletion of the ground state of the antenna in **Dyad-1**. Besides the bleaching bands, positive transients at 400, 550, 650, and 800 nm were found. These positive transient bands can be assigned to the absorption of the triplet state of the styryl Bodipy antenna in **Dyad-1**. This conclusion was confirmed by the transient absorption of **B-4**, which gives a similar transient absorption profile (SI). The transient absorption of **B-8** cannot be determined due to the lack of heavy atoms in the molecule; thus the triplet excited state cannot be efficiently produced.

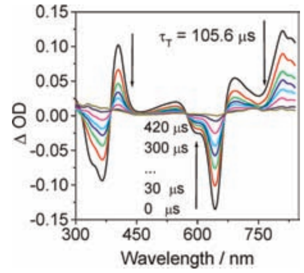

Figure 3. Nanosecond time-resolved transient absorption of **Dyad-1**. In deaerated toluene. Excited at 532 nm, 20 °C.

Thus, the T_1 excited state of **Dyad-1** is localized on the styryl-Bodipy antenna, not on the C_{60} moiety. The energy level of the T_1 state of the antenna (1.06 eV), much lower than the T_1 state of C_{60} (1.73 eV), imparts the triplet state energy transfer from C_{60} to the styryl-Bodipy unit. The lifetime of the triplet excited state of **Dyad-1** was determined to be 105.6 μs. Note the T_1 state lifetime of C_{60} alone is only 40.6 μs (Table 1).

In order to study the localization of the T_1 state of the dyads, the spin densities of the dyads were calculated (Figure 4). The spin density is exclusively localized on the styryl-Bodipy unit. The C_{60} unit does not contribute to the spin density, which fully coincides with the time-resolved transient absorption spectra (Figure 3). Similar results were found for **Dyad-2** (SI).

Triplet photosensitizers can be used for photodynamic therapy (PDT) or photooxidation via sensitizing $^1O_2$.[30] Ir(III) complexes have been used for the photooxidation of DHN (Figure 5).[30] Herein **Dyad-1–3** were used as organic triplet photosensitizers for the photooxidation of DHN (the photooxidation product is juglone).

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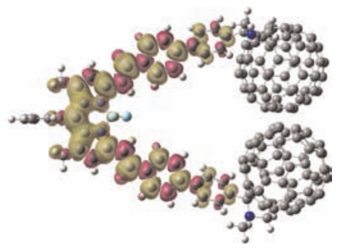

Figure 4. Spin density surface of **Dyad-1**. Calculated at B3LYP/6-31G(d) level with Gaussian 09W.

Table 1. Photophysical Parameters of the Dyads[a]

	λ_{abs}	ε	λ_{em}	Φ^b	$\tau_T{}^c$/ μs	$\tau_F{}^d$/ ns
Dyad-1	645	5.68	662	0.01	105.6	–
Dyad-2	629	6.53	644	0.01	71.5	–
Dyad-3	657	6.46	667	0.009	123.2	–
B-4	635	9.08	647	0.53	2.6	4.4
B-8	629	12.0	641	0.59	–	4.6
C_{60}	335	4.73	720	–	40.6	–

[a] In toluene at 20 °C. [b] With **B-8** (Φ_F = 0.59 in toluene) as the standard. [c] Triplit state lifetimes. [d] Fluorescence lifetimes.

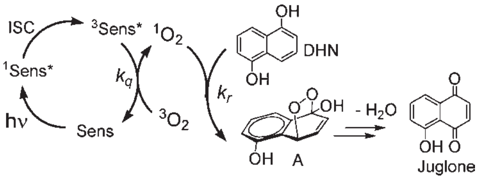

Figure 5. Photooxidation of DHN with triplet photosensitizer.

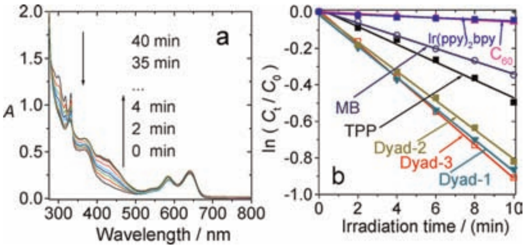

Figure 6. Absorption change in the photooxidation of DHN. (a) **Dyad-1** as sensitizer. (b) Plots of ln(C_t/C_o) vs irradiation time. c[sensitizers] = 5.0×10^{-6} M. c[DHN] = 1.0×10^{-4} M. In CH_2Cl_2/MeOH (9:1, v/v); 20 mW cm^{-2}; 20 °C.

The consumption of DHN can be monitored by the decrease in its absorption at 301 nm. The change is significant with C_{60} dyads as photosensitizers (Figure 6a). The photooxidation rate constant of **Dyad-1** compared to the traditional organic triplet photosensitizer tetraphenylporphyrin (TPP) and methylene blue (MB) increased 1.7-fold. The k_{obs} value of **Dyad-1** compared to **Ir-1** is ca. 20-fold higher (Table 2). In comparison, C_{60} gives much slower photooxidation kinetics, due to its poor absorption of visible light. Thus in this case, the visible light-harvesting C_{60} dyads are more useful than C_{60}.

Table 2. Pseudo-First-Order Kinetics Parameters, and Yields of Juglone for the Photooxidations of DHN Using Different Triplet Photosensitizers

	$k_{obs}{}^a$/ min^{-1}	$v_i{}^b$	yield^c/ %	$\Phi_\Delta{}^d$
Dyad-1	86	8.6	99.9	0.85
Dyad-2	82	8.2	99.9	0.82
Dyad-3	91	9.1	99.9	0.85
B-4	6.3	0.63	11.6	–
TPP	50	5.0	99.9	0.62^e
MB	34	3.4	66.0	0.57
C_{60}	5.7	0.57	30.0	0.76^e
Ir(ppy)$_2$bpy	4.5	0.45	27.0	–

[a] Photoreaction rate constants; 10^{-3} min^{-1}. [b] Initial rate; 10^{-5} M. In min^{-1}. [c] Yield of Juglone after photoirradiation for 30 min. [d] Quantum yield of singlet oxygen ($^1O_2$), with methylene blue (MB) as standard (Φ_Δ = 0.57 in CH_2Cl_2). [e] Literature values.[35]

In conclusion, styryl Bodipy-C_{60} dyads were prepared as organic triplet photosensitizers. The dyads show strong absorption of red light and long-lived triplet excited states. Upon photoexcitation, the triplet excited state localized on the antenna was populated via a "ping-pong" intramolecular energy transfer between the antenna and the C_{60} unit. The dyads were used as singlet oxygen ($^1O_2$) photosensitizers, and the photosensitizing efficiency of the dyads compared to the known Ir(III) complex triplet photosensitizer increased ca. 20-fold. We propose the C_{60}-organic chromophore dyads can be used as a *general* structure motif for *heavy-atom-free organic* triplet photosensitizers, for which the absorption can be readily changed by using different antennas, and the ISC property is fully predictable.

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Supporting Information Available. General experimental methods, ^{1}H NMR, absorption and emission spectra of **Dyad-2** and **-3**. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.