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Light-Harvesting Fullerene Dyads as Organic Triplet Photosensitizers for Triplet–Triplet Annihilation Upconversions

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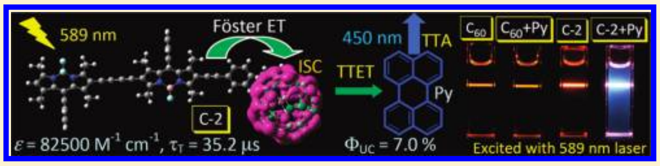
Supporting Information



ABSTRACT: Visible light-harvesting C_{60}–bodipy dyads were devised as universal organic triplet photosensitizers for triplet–triplet annihilation (TTA) upconversion. The antennas in the dyad were used to harvest the excitation energy, and then the singlet excited state of C_{60} will be populated via the intramolecular energy transfer from the antenna to C_{60} unit. In turn with the intrinsic intersystem crossing (ISC) of the C_{60}, the triplet excited state of the C_{60} will be produced. Thus, without any heavy atoms, the triplet excited states of organic dyads are populated upon photoexcitation. Different from C_{60}, the dyads show strong absorption of visible light at 515 nm (**C-1**, ε = 70400 M^{-1} cm^{-1}) or 590 nm (**C-2**, ε = 82500 M^{-1} cm^{-1}). Efficient intramolecular energy transfer from the bodipy moieties to C_{60} unit and localization of the triplet excited state on C_{60} were confirmed by steady-state and time-resolved spectroscopy as well as DFT calculations. The dyads were used as triplet photosensitizers for TTA upconversion, and an upconversion quantum yield up to 7.0% was observed. We propose that C_{60}–organic chromophore dyads can be used as a general molecular structural motif for organic triplet photosensitizers, which can be used for photocatalysis, photodynamic therapy, and TTA upconversions.

1. INTRODUCTION

Upconversions have attracted much attention because of their applications in photovoltaics, photocatalysis, photoinduced charge separation, and molecular probes.[1−13] Among the upconversion methods, such as using rare earth metal materials[1,2] and two-photon-absorption dyes,[3,4] the triplet–triplet annihilation (TTA) upconversion is particularly interesting[5−7] for its advantages over the conventional upconversion methods.[5−13] For example, TTA upconversion requires noncoherent low-power excitation, and it shows intense absorption of the excitation light as well as high upconversion quantum yields.[5a,6,7a]

Triplet photosensitizers and triplet acceptors (annihilator, emitter) are used in TTA upconversion.[5a,6,7a] The photosensitizers are selectively photoexcited in the presence of triplet acceptor, and then the triplet excited states of the photosensitizers are populated, via the intersystem crossing (ISC) effect, very often exerted by heavy atoms such as Pt(II), Ir(III), or iodine substituents.[5a,6,7a] The photoexcitation energy migrates to the triplet acceptor from the photosensitizer by the triplet–triplet energy-transfer (TTET) process. Then the TTA between the triplet acceptors produces the singlet excited state, and the delayed fluorescence (upconverted fluorescence) can be observed (for the photophysical mechanism, see Scheme 2).[5a,6,7a]

Currently, the challenge for the development of TTA upconversion is the limited availability of the triplet photosensitizers.[6] Usually the sensitizers are phosphorescent transition-metal complexes, such as Pt(II)/Pd(II) porphyrin complexes,[14−17] Ru(II) polyimine complexes,[11,12,18] cyclometalated Pt(II) complexes,[10,19,20] Ir(III) complexes,[8,21] and Pt(II) acetylide complexes.[22,23] However, the photophysical properties of these complexes cannot be readily optimized and they are not cost-effective. Therefore, similar to the scenario of the dye-sensitized solar cells,[24−27] to replace the transition metal complex sensitizers with organic triplet photosensitizers will be the next milestone for TTA upconversion.

Unfortunately, it is challenging to prepare organic triplet photosensitizers because the ISC is very often nonefficient without the heavy atom effect of Pt, Ir, Ru, and I.[28] Only sporadic examples of organic triplet sensitizers for TTA upconversion have been reported, such as 2,3-butanedione[29] and 2,4,5,7-tetraiodo-6-hydroxy-3-fluorone.[30a] Eosin and the derivatives have also been used as triplet sensitizers in photochemical reactions.[30b] However, these organic triplet photosensitizers suffer from disadvantages of either short excitation wavelength (in UV range) or resorting to heavy atom effect (iodo atom), and it is difficult to functionalize the molecular structures to tune the photophysical properties.[6] Recently, we prepared organic triplet photosensitizers based on boron–dipyrromethene (BODIPY) and naphthalenediimide (NDI) that shows tunable absorption wavelength.[13] However, the heavy atom effect is still mandatory for these organic triplet photosensitizers.[13] Since it is not always convenient to prepared iodated organic chromophore, and the ISC property of the iodated chromophore cannot be guaranteed, we set out to prepare organic triplet photosensitizers without any heavy atoms. However, without the heavy atom effect, it becomes

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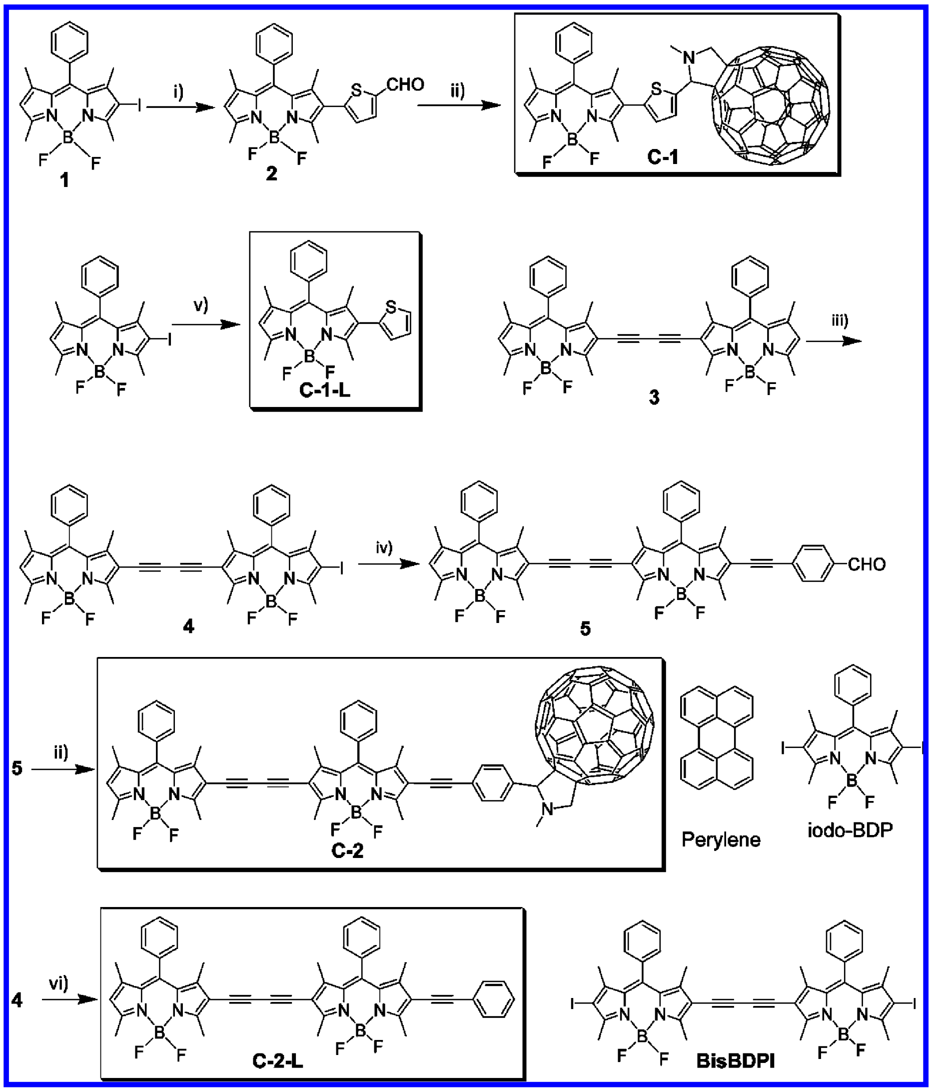
Scheme 1. Synthesis of the C_{60}-Based Dyads C-1 and C-2 as Organic Triplet Sensitizers and Light-Harvesting Antennas C-1-L and C-2-L[a,b]



[a] The structures of perylene (triplet acceptor in the upconversion) and **iodo-BDP** and **BisBDPI** used as the standard of upconversion quantum yield were also shown.

[b] Key: (i) 5-formyl-2-thiopheneboronic acid, $Pd(OAc)_2$, H_3PO_4; (ii) sarcosine, C_{60}, toluene, reflux; (iii) NIS, CH_2Cl_2, 40 °C; (iv) 4-ethynylbenzaldehyde, $Pd(PPh_3)_2Cl_2$, PPh_3, CuI, THF/Et_3N; (v) 2-thiopheneboronic acid, $Pd(OAc)_2$, H_3PO_4; (vi) phenylacetylene, $Pd(PPh_3)_2Cl_2$, PPh_3, CuI, THF/Et_3N.

almost impossible to predict whether or not an organic chromophore will undergo ISC upon photoexcitation.

Herein, we propose a *universal* strategy to address this challenge, that is, to use the light-harvesting organic fluorophore–fullerene (C_{60}) dyads as a general molecular structure motif for the heavy atom free organic triplet photosensitizers. These dyads show strong absorption of visible light, and the molecular structure can be readily changed by using different light-harvesting antennas. More importantly, the population of the triplet excited states of these dyads upon photoexcitation is predetermined. Thus, design of organic triplet photosensitizers will become feasible. The C_{60}–bodipy dyads were used for TTA upconversion (**C-1** and **C-2**, Scheme 1), and significant upconversion quantum yields were observed.

2. RESULTS AND DISCUSSION

2.1. Design and Synthesis of the C_{60}–bodipy Dyads.

C_{60} is used as the intramolecular energy acceptor and the *spin convertor*, because of its intrinsic capability of ISC, with which the triplet excited state of C_{60} can be efficiently populated, without resorting to heavy atom effect (the quantum yield of the triplet excited state of C_{60} upon photoexcitation is close to unity).[31−34] It should be noted that the visible light-harvesting bodipy units in dyads **C-1** and **C-2** (the intramolecular energy *donor*) are mandatory because C_{60} alone gives a very weak absorption in the visible range.[31,32,35] C_{60} has been extensively studied in organic solar cells, supramolecular chemistry,[36] but its ISC capability in a C_{60}–organic chromophore dyad has rarely been explored for sensitizing a photophysical process.[35c] Previously, fluorene–C_{60} dyads was reported for singlet oxygen sensitizing, but dyads show moderate absorption in visible range.[35c] The delayed fluorescence of C_{70} was used for O_2

sensing.[34a] In order to enhance the absorption of the C_{60} dyads in the visible range, bodipy was selected as the light-harvesting antenna because of its ideal photophysical properties, such as strong absorption of visible light, good photostability, and derivatizable molecular structures.[37,38]

Thienyl-substituted bodipy **C-1-L** shows strong absorption of visible light.[38] The excitation energy harvested by the Bodipy antennas can be transferred to C_{60} via the Föster mechanism. The triplet state of C_{60} will be populated via its intrinsic ISC capability (the efficiency is up to 95%).[32] Thus, **C-1** can be used as an *organic* triplet photosensitizer, which is without any transition metal atoms or heavy atoms such as Pt(II), Ir(III), or iodine atoms. Similar rationales are applicable to **C-2**, in which the bis-Bodipy **C-2-L** moiety shows red-shifted absorption compared to that of **C-1-L**.

The preparation of the antenna is based on Suzuki or Sonogashira cross coupling. Because of the versatile derivatization of bodipy, the π-conjugation framework is readily extended. Thus, the absorption can be moved to the red range of the spectrum (**C-2-L**). The antenna was attached to the C_{60} unit by a Prato reaction. All of the compounds were obtained in moderate to satisfying yields (see the Experimental Section for details).

2.2. UV−vis Absorption and Fluorescence Spectra of the Compounds.

An intense absorption at 513 nm is found for **C-1-L** (ε = 69000 M^{-1} cm^{-1}) (Figure 1a). Conversely, C_{60} alone shows very weak absorption at 513 nm (e.g., ε = 1230 M^{-1} cm^{-1}). However, an intense absorption at 515 nm (ε = 70400 M^{-1} cm^{-1}) is observed for the dyad **C-1**, which is the sum of C_{60} and **C-1-L**, indicates no significant electronic communication between the energy donor (bodipy unit) and acceptor (C_{60} unit) at the ground state.

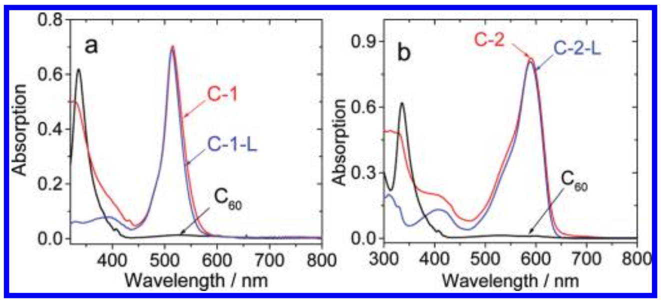


Figure 1. UV−vis absorption spectra of (a) **C-1** and (b) **C-2** and the antennas of the dyads. c = 1.0 × 10^{-5} M in toluene, 20 °C.

Similar results were observed for **C-2** (Figure 1b). **C-2-L** unit gives red-shifted absorption at 589 nm compared to **C-1-L**. Similar to **C-1**, the absorption of **C-2** is the sum of **C-2-L** and C_{60} (Figure 1b).

C_{60} *does* show weak absorption beyond 500 nm, which is *crucial* for the intramolecular energy transfer from bodipy to C_{60} unit. The weak absorption of C_{60} in the visible range indicates weakly allowed $S_0 \rightarrow S_n$ transitions, but it *does not* necessarily mean that the intramolecular energy transfer from the bodipy antenna to C_{60} is *weakly* allowed. On the contrary, efficient energy transfers from the energy donors (bodipy) in **C-1** and **C-2** to C_{60} units were observed (Figure 2).

The photoinduced intramolecular energy transfer of dyads **C-1** and **C-2** was confirmed by the luminescence study (Figure 2). The **C-1-L** alone gives intense fluorescence at 594 nm (Φ_F = 20.6%). For C_{60}, however, no emission was observed with excitation at 510 nm under the same conditions. This lack of emission is due to the extremely weak absorption of C_{60} at 510 nm as well as its low fluorescence quantum yield (Φ_F < 0.1%).[31,32]

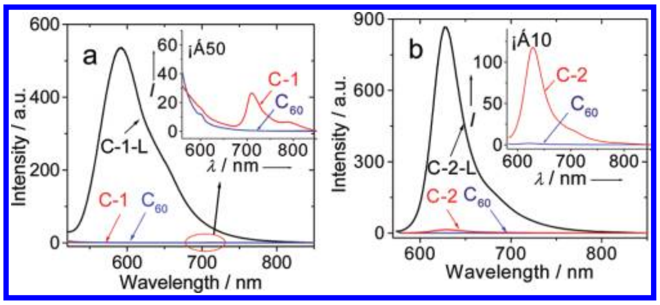


Figure 2. (a) Fluorescence emission spectra of **C-1-L**, **C-1**, and C_{60} (λ_{ex} = 510 nm). (b) Fluorescence emission spectra of **C-2-L**, **C-2**, and C_{60}. In toluene, λ_{ex} = 570 nm, 1.0 × 10^{-5} M, 20 °C.

Dyad **C-1** is weakly fluorescent at 594 nm (**C-1-L** gives strong emission). Emission at 710 nm was observed for **C-1**, which can be assigned to the emission of C_{60} unit. These two observations are clear indications of the intramolecular energy transfer from bodipy to the C_{60} unit in **C-1**. The intramolecular energy transfer is efficient because the fluorescence emission of **C-1-L** is completely quenched in **C-1**. Similar studies were carried out for **C-2** (Figure 2b). However, determination of the exact energy transfer efficiency is not straightforward,[37] although the quenched fluorescence of the energy donor were used for the determination of the energy transfer efficiency in some cases. However, the nonemissive excited state of the energy donor (antenna) was not considered with this method.

We found that similar intramolecular energy transfer also occurs for **C-2** (Figure 2b). The fluorescence of **C-2-L** was significantly quenched in dyad **C-2** (Figure 2b), which indicates efficient energy transfer from bis-bodipy to C_{60} moiety. Emission of C_{60} in **C-2** is probably buried in the residual emission of **C-2-L**. The photophysical properties of the compounds are summarized in Table 1.

Table 1. Photophysical Parameters of the C_{60} Dyads and the Components[a]

	λ_{abs}	ε[b]	λ_{em}	Φ_F[c] (%)	τ
C_{60}	336	6.19			40.6 μs[e]
C-1-L	513	6.90	594	20.6	3.2 ns[f]
C-2-L	589	8.08	627	62.0	1.7 ns[f]
C-1	515	7.04	710		33.3 μs[e]
C-2	590	8.25	627	1.7[d]	35.2 μs[e]

[a] In toluene (1.0 × 10^{-5} M). [b] Molar extinction coefficient at the absorption maxima. ε: 10^4 M^{-1} cm^{-1}. [c] With 1,3,5,7-tetramethyl-8-phenyl-4-bora-3a,4a-diaza-*s*-indacene as the standard (Φ = 72.0% in THF). [d] With 2,6-diiodo-4,4-difluoro-1,3,5,7-tetramethyl-8-phenyl-4-bora-3a,4a-diaza-*s*-indacene (Iodo-BDP in Scheme 1) as the standard (Φ = 2.7% in MeCN). [e] Triplet state lifetimes, measured by transient absorptions. [f] Fluorescence lifetimes.

2.3. Nanosecond Time-Resolved Transient Difference Absorption Spectroscopy.

In order to confirm the population of the triplet excited state of the dyads upon photoexcitation, nanosecond time-resolved transient difference absorption spectroscopy were studied (Figure 3). Significant transient absorption at 720 nm was observed for **C-1** upon pulsed excitation, which is the characteristic absorption of the

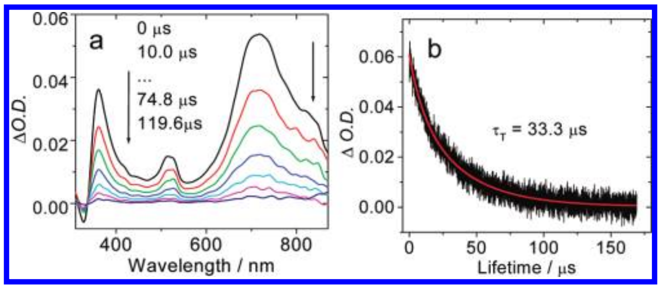


Figure 3. (a) Nanosecond time-resolved transient difference absorption spectra of **C-1** (λ_{ex} = 532 nm). (b) Decay traces of the transient absorption of **C-1** at 720 nm. In deaerated toluene, 25 °C.

triplet excited state of C_{60}.[32a] No bleaching of the bodipy unit at 515 nm was found, where the ground state of bodipy shows strong absorption, indicating that the triplet excited state of the dyad is exclusively localized on C_{60}, not on the bodipy unit. We attribute this C_{60}-localized triplet state to the lower T_1 state energy level of C_{60} (1.50 eV)[39] rather than **C-1-L** (1.51 eV, approximated by DFT calculations). The transient was significantly quenched in aerated solution, which confirms its triplet-state feature, excluding formation of intramolecular charge-transfer species (Figure S21, Supporting Information).[32a] The lifetime of the triplet excited state of the dyad was determined to be 33.3 *μ*s by monitoring the decay kinetics at 720 nm (Figure 3), which is slightly shorter than the triplet excited state lifetime of the unsubstituted C_{60} (40.6 *μ*s) (Table 1).[31,40]

Similar transient absorption spectra were observed for **C-2** (Figure S23, Supporting Information). A C_{60}-localized T_1 excited state was observed for **C-2** (τ_T = 35.2 *μ*s, Figure S23, Supporting Information, and Table 1). It is remarkable that the energy level of the T_1 state of **C-2-L** is not significantly decreased compared to that of **C-1-L**, indicated by the localization of the triplet excited state on C_{60} unit, not the **C-2-L** unit in **C-2**, although the absorption of **C-2** is red-shifted by **76** nm vs **C-1-L**. This high T_1 state energy level may be due to the unique distribution of the spin density of the T_1 state of a similar chromophore; that is, the spin density is localized on one of the two Bodipy units of the antenna.[13a] In other words, the limited *π*-conjugation of the T_1 state, not fully delocalized in the *π*-conjugation framework of the chromophore, is responsible for the apparently high T_1 state energy level of the antenna **C-2-L** in **C-2**.[13a]

2.4. Spin Density Analysis of the Dyads.

In order to confirm the C_{60}-localized T_1 state of the dyads, the spin density surfaces were studied (Figure 4). For both **C-1** and **C-2**, the spin densities are exclusively localized on C_{60}, and the light-harvesting bodipy does not contribute to the spin density surfaces. This result is in full agreement with the transient difference absorption spectroscopy (Figure 3 and Figure S23, Supporting Information).

2.5. C_{60}–bodipy Dyads as Organic Triplet Photosensitizers for TTA Upconversion.

The C_{60} dyads **C-1** and **C-2** were used as organic triplet photosensitizers for TTA upconversion (Figure 5, perylene as the triplet acceptor).[5a,6,7a]

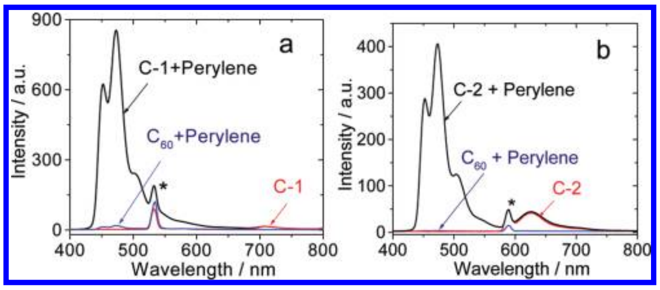


Figure 5. TTA upconversion with (a) **C-1** (λ_{ex} = 532 nm) and (b) **C-2** (λ_{ex} = 589 nm) as the triplet photosensitizers (1.0 × 10^{-5} M) and perylene as the acceptor (4.1 × 10^{-4} M). The asterisks in (a) and (b) indicate the scattered laser. In toluene. Excited with CW lasers (532 and 589 nm), 12 mW, 20 °C.

For **C-1**, weak fluorescence of C_{60} was observed at 710 nm upon laser excitation. Upon addition of perylene, an intensive blue emission at 470 nm was observed. Irradiation of perylene alone at 532 nm did not produce this emission band, thus the upconversion with **C-1**/perylene is confirmed. The upconversion quantum yield (Φ_{UC}) with **C-1** was determined as 2.9% (Table 2). This value is significant considering the intense

Table 2. Triplet Excited-State Lifetimes (τ_T), Stern–Volmer Quenching Constant (K_{SV}), and Bimolecular Quenching Constants (k_q) of the Chromophore/C_{60} Dyads[a]

	τ_T (*μ*s)	K_{sv} (10^4 M^{-1})	k_q (10^9 M^{-1} s^{-1})	Φ_{UC} (%)	η[d]
C-1	33.3	3.19	0.96	2.9[b]	1303
C-2	35.2	4.40	1.25	7.0[c]	5769
C_{60}	40.6	1.01	0.25	2.4[b]	30.9
BisBDPI	26.9	28.9	10.7	11.3[b]	6171

[a] Perylene was used as the quencher. In deaerated toluene solution, 20 °C. [b] Excited with 532 nm laser, with the prompt fluorescence of 2-iodo-4,4-difluoro-1,3,5,7-tetramethyl-8-phenyl-4-bora-3a,4a-diaza-*s*-indacene as the standard (compound **iodo-BDP** in Scheme 1. Φ = 2.7% in MeCN). [c] Excited with 589 nm laser, with the prompt fluorescence of **BisBDPI** (Scheme 1) as the standard (Φ = 10.5% in toluene). [d] Overall upconversion capability,[6] $\eta = \varepsilon \times \Phi_{UC}$, where ε is the molar extinction coefficient of the triplet photosensitizer at the excitation wavelength and Φ_{UC} is the upconversion quantum yield.[5a] In M^{-1} cm^{-1}.

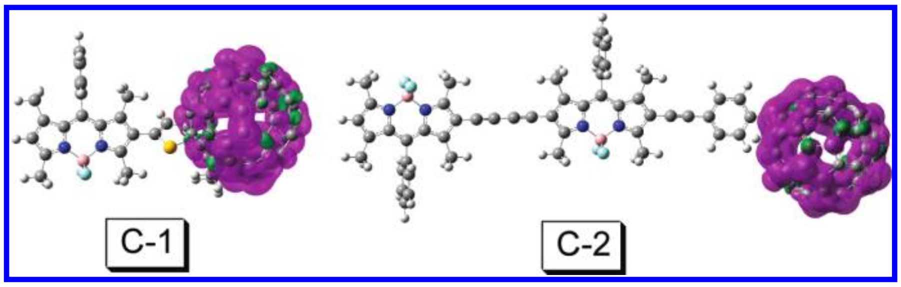


Figure 4. Spin-density surface of **C-1** and **C-2** at the triplet state. Calculated at B3LYP/6-31G(d) level with Gaussian 09W.

absorption of **C-1**,[6] since the overall upconversion capability can be more precisely evaluated by $\eta = \varepsilon \times \Phi_{UC}$ (ε is the molar extinction coefficients of the sensitizer),[6] instead of the Φ_{UC} value alone.[5a] C_{60} alone as the sensitizer also shows upconversion (Φ_{UC} = 2.4%). However, C_{60} shows very weak absorption at 532 nm (ε = 1289 M^{-1} cm^{-1}); thus, the η value of C_{60} ($\eta = \varepsilon \times \Phi_{UC}$ = 30.9 M^{-1} cm^{-1}) is at least 40-fold *weaker* than that of **C-1** ($\eta = \varepsilon \times \Phi_{UC}$ = 44960 M^{-1} cm^{-1} × 2.9% = 1303 M^{-1} cm^{-1}).

C-2 shows red-shifted absorption (590 nm). Significant upconversion was observed with **C-2** (Figure 5b, λ_{ex} = 589 nm). The Φ_{UC} was determined as 7.0% (Table 2). Interestingly, with C_{60} as the sensitizer no upconversion was observed with excitation at 589 nm laser, due to the much weaker absorption of C_{60} at 589 nm. These results demonstrated that the light-harvesting of the dyads is crucial for TTA upconversion with the C_{60} dyads. Upconversion with **C-1** and **C-2** are visible with the unaided eye (Figure 6a and 6b). Both **C-1** and **C-2** are photostable, and no bleaching was observed (Figure S29, Supporting Information). We noted that the TTA upconversions of C-1 and C-2 are comparable to those of iodo-Bodipys.[13a]

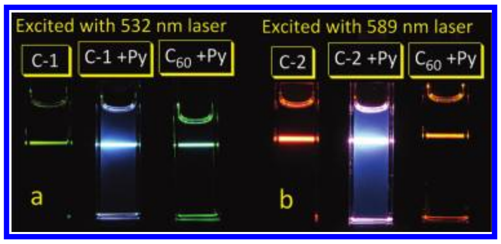


Figure 6. Photographs of the emissions of triplet sensitizers alone and the upconversion. TTA upconversion with (a) **C-1** (λ_{ex} = 532 nm) and (b) **C-2** (λ_{ex} = 589 nm) as the triplet photosensitizers (1.0 × 10^{-5} M) and perylene as the triplet acceptor (4.1 × 10^{-4} M). In toluene. Excited with CW lasers, 12 mW, 20 °C.

In order to unambiguously confirm that the blue emission observed for the mixed solution of dyads and the acceptor perylene (Figure 5) is due to the TTA upconversion, the lifetime of the upconverted emission was measured (Figure 7).

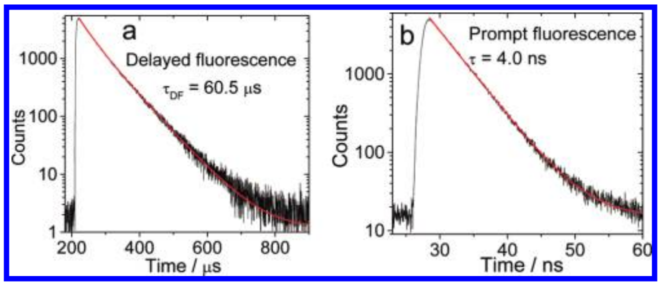


Figure 7. (a) Delayed fluorescence observed in the TTA upconversion with compound **C-1** as triplet photosensitizer and perylene as the triplet acceptor. Excited at 532 nm (nanosecond pulsed OPO laser synchronized with spectrofluorometer) and monitored at 470 nm. Under this circumstance, the compound **C-1** is selectively excited and the emission is due to the upconverted emission of perylene. In deaerated toluene. *c*[sensitizers] = 1.0 × 10^{-5} M; *c*[perylene] = 4.1 × 10^{-4} M; 20 °C. (b) The prompt fluorescence decay of perylene determined in a different experiment (excited with picosecond 405 nm laser, the decay of the emission was monitored at 470 nm), *c*[perylene] = 1.0 × 10^{-5} M; 20 °C.

The lifetime of the emission for **C-1**/perylene was determined as 60.5 μs. In a different experiment, the lifetime of the prompt fluorescence of perylene alone was determined as 4.0 ns. Thus, the exceptionally long-lived fluorescence of perylene in the presence of **C-1** (15000-fold of the prompt fluorescence lifetime of perylene) can be assigned to the TTA upconversion, i.e., the delayed fluorescence.[9d] Similar results were found for **C-2**/perylene; in this case, the lifetime of the delayed fluorescence of perylene was determined as 61.2 μs (see Figure S28, Supporting Information). These time-resolved emission studies of the samples in Figure 5 unambiguously demonstrated that the emission is due to the TTA upconversion.

The triplet−triplet energy transfer (TTET) of the TTA upconversion were studied by monitoring the quenching of the triplet state lifetimes of the dyads by the triplet acceptor perylene (Figure 8).[5a,6] Smaller K_{SV} values for **C-1** (K_{SV} = 3.19 × 10^4 M^{-1}) and **C-2** (K_{SV} = 4.40 × 10^4 M^{-1}) were observed compared to that of the **BisBDPI** (Scheme 1), which has a shorter τ_T value (K_{SV} = 2.89 × 10^5 M^{-1}, Table 2). Usually, photosensitizers with a long-lived triplet excited state should give high TTET quenching constants. The apparently smaller K_{SV} values of **C-1** and **C-2** may be due to the large molecular size of the C_{60} dyads compared to BisBDPI (Scheme 1). Large molecular size may make the diffusion of the sensitizers in solution much slower. Furthermore, the distribution of the spin density on the bulky spherical C_{60} moiety may also make the TTET process less efficient. However, the TTA upconversion performance with the C_{60} dyads are not compromised, due to the versatility of the C_{60} dyads, such as the feasibly tunable molecular structure, strong absorption of visible light, long-lived triplet excited state, and most importantly the heavy atom-independent predetermined ISC capability.

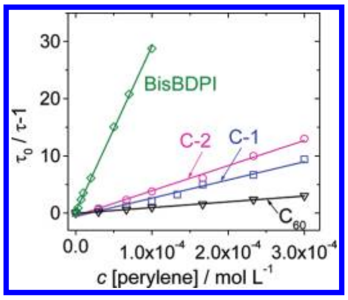
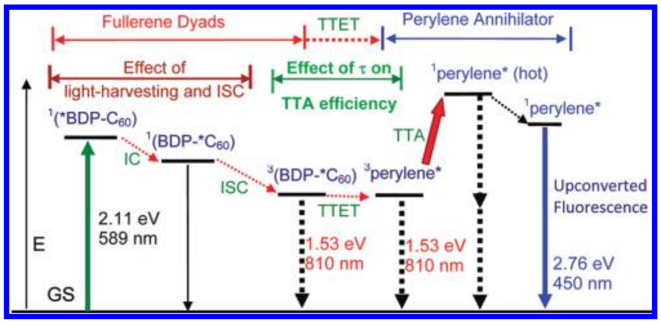


Figure 8. Stern−Volmer plots generated from the triplet excited-state lifetime (τ_T) quenching curves of the compounds measured as a function of perylene concentration. In toluene, 20 °C.

The photophysical processes involved in the TTA upconversion with the C_{60} dyads as the triplet photosensitizer are summarized in Scheme 2, exemplified with **C-2**. First, the singlet excited state of the bodipy antenna in **C-2** was populated upon photoexcitation (589 nm). Then the intramolecular Föster energy transfer from the antenna to the C_{60} unit will produce the singlet excited state of C_{60}. With the intrinsic ISC property of C_{60}, the triplet excited state of C_{60} was populated. With time-resolved spectroscopy and the spin density surface analysis, we proved that the triplet excited state of dyad **C-2** is localized on C_{60}. The TTET between the **C-2** and the triplet acceptor perylene will produce the triplet excited state of the acceptors. TTA will give acceptor molecules at the singlet excited states. Radiative decay from the singlet excited state produces the upconverted fluorescence (delayed fluorescence). From these processes, it is clear that the light-

Scheme 2. Jablonski Diagram of Photophysics of the C_{60}–bodipy Dyads and the Application of Dyads as Triplet Photosensitizers for Triplet–Triplet Annihilation (TTA) Upconversion Triplet States of the Sensitizers and Acceptors Are Nonemissive)[a]



[a]Exemplified with **C-2** as the triplet photosensitizer. The effect of the light-harvesting ability and the lifetimes of the sensitizers on the efficiency of TTA upconversion are shown (please note that the vibration energy levels of each electronic state are omitted for clarity). *E* is energy. GS is ground state (S_0). ^{1}(*BDP-C_{60}) is singlet excited state localized on BDP, and ^{1}(BDP-*C_{60}) is singlet excited state localized on fullerene. IC is inner conversion. ISC is intersystem crossing. ^{3}(BDP-*C_{60}) is the triplet excited state localized on fullerene. TTET is triplet–triplet energy transfer. ^{3}perylene* is the triplet excited state of perylene. TTA is triplet–triplet annihilation. ^{1}perylene* is the singlet excited state of perylene (initially the hot, or the vibrationally excited S_1 state will be populated). The emission band observed in the TTA experiment is the ^{1}perylene* emission (fluorescence). The typical power density of the laser used in the upconversion is 170 mW cm^{-2}, too low to observe simultaneous two-photon absorption.

harvesting ability of the antenna, the lifetime of the triplet excited state of the dyad, and the TTA efficiency are the main factors that influence the performance of TTA upconversion.

2.6. Conclusions. In conclusion, visible light-harvesting C_{60} dyads were devised as a general molecular structure motif for heavy atom-free organic triplet photosensitizers. The dyads are based on visible light-harvesting organic chromophores (energy donor, herein it is bodipy) and the *spin converter* C_{60} (energy acceptor). Different from C_{60}, the dyads show strong absorption of visible light (at 515 and 590 nm, respectively). Steady-state luminescence indicated efficient intramolecular energy transfer from the bodipy antenna to the C_{60} energy acceptor. Nanosecond time-resolved transient absorption and spin density analysis proved that the triplet excited states of the dyads are localized on the C_{60} moieties. The dyads were used as triplet organic photosensitizers for triplet–triplet annihilation upconversion, and quantum yield up to 7.0% was observed. Our results pave the way for design of heavy atom-free organic triplet photosensitizers with the predetermined intersystem crossing property. To replace the currently used phosphorescent transition-metal complex, triplet photosensitizers with these heavy atom free C_{60} dyads as organic triplet photosensitizers will exert substantial impact in the areas such as TTA upconversion, photocatalysis, photovoltaics, and photodynamic therapy reagents (PDT).

3. EXPERIMENTAL SECTION

3.1. General Methods. Fluorescence lifetimes were measured on an OB920 luminescence lifetime spectrometer. The nanosecond time-resolved transient absorption spectra were detected by an LP920 laser flash photolysis spectrometer. The transient signals were recorded on a digital oscilloscope. The lifetime values (by monitoring the decay trace of the transients) were obtained with LP900 software. All samples in flash photolysis experiments were deaerated with Ar for ca. 15 min before measurement, and the gas flow was maintained during the measurements. Syntheses of compounds **1** and **3** were reported elsewhere.[13a]

3.2. Synthesis of Compound 2. Under Ar atmosphere, 5-formyl-2-thiopheneboronic acid (102.9 mg, 0.66 mmol) was added to the solution of compound **1** (100.0 mg, 0.22 mmol) in toluene (5 mL) and ethanol (5 mL), and after thorough mixing, $K_3PO_4 \cdot 3H_2O$ (117.2 mg, 0.44 mmol) and Pd(OAc)$_2$ (2.6 mg, 0.013 mmol) were added. The mixture was heated to 80 °C and was allowed to reflux for 8 h. After complete consumption of the starting material, the solvents were evaporated under reduced pressure, and the crude product was further purified using column chromatography (silica gel, CH_2Cl_2/hexane = 1:1, v/v) to give **2** as a red power (40.0 mg). Yield: 41.9%. Mp: 173.2–174.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 9.87 (s, 1H), 7.73 (d, 1H, *J* = 3.7 Hz), 7.52 (d, 3H, *J* = 5.1 Hz), 7.31 (d, 2H, *J* = 5.6 Hz), 6.95 (d, 1H, *J* = 3.6 Hz), 6.07 (s, 1H), 2.62 (s, 3H), 2.60 (s, 3H), 1.40 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 191.7, 158.0, 155.8, 155.3, 137.9, 137.5, 131.7, 130.4, 130.3, 114.7, 113.0, 96.8, 46.5, 12.9. MALDI-HRMS: calcd ([$C_{24}H_{21}BF_2N_2OS$]$^+$) *m*/*z* = 434.1436, found *m*/*z* = 434.1436.

3.3. Synthesis of Compound 4. *N*-Iodosuccinimide (NIS) (140 mg, 0.62 mmol) in dry CH_2Cl_2 (10 mL) was added dropwise into a solution of compound **4** (200 mg, 0.62 mmol) in CH_2Cl_2 (50 mL) within ca. 1 h at rt. After the addition, the reaction mixture was stirred at 40 °C overnight. The reaction mixture was then concentrated under reduced pressure, and the crude product was purified by column chromatography (silica gel, hexane/CH_2Cl_2, 2:1, v/v). The second band was collected to give the product as a purple solid (191.7 mg). Yield: 68.7%. Mp: >250 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 7.53–7.49 (m, 6H), 7.26–7.23 (m, 4H), 6.06 (s, 1H), 2.65 (s, 9H), 2.58 (s, 3H), 1.44 (s, 6H), 1.40 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 159.5, 158.9, 157.7, 157.6, 146.1, 145.7, 144.0, 142.2, 134.5, 133.1, 132.4, 130.4, 129.9, 129.6, 129.5, 127.9, 127.8, 127.7, 115.1, 113.6, 86.2, 80.9, 80.1, 76.1, 75.0, 17.1, 14.8, 13.6, 13.3. MALDI-HRMS: calcd ([$C_{42}H_{35}B_2F_4N_4I$]$^+$) *m*/*z* = 820.2029, found *m*/*z* = 820.2050.

3.4. Synthesis of Compound 5. Under N_2 atmosphere, compound **4** (40.0 mg, 0.05 mmol), 4-ethynylbenzaldehyde (13.0, 0.10 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (3.5 mg, 0.005 mmol), PPh$_3$ (2.6 mg, 0.01 mmol), and CuI (2.0 mg, 0.01 mmol) were dissolved in a mixed solvent of THF/Et$_3$N (3 mL/2 mL), and the flask was vacuumed and backfilled with Ar several times. The mixture was heated at 50 °C for 6 h. The solvent was removed, and the crude product was purified by column chromatography (silica gel, hexane/CH_2Cl_2, 2:1, v/v). The dark purple band was collected, and evaporation of solvent gave a blue solid (35.1 mg). Yield: 85.5%. Mp: >250 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 10.00 (s, 1H), 7.85 (d, 2H, *J* = 7.8 Hz), 7.59 (d, 2H, *J* = 8.0 Hz), 7.54–7.50 (m, 6H), 7.26 (m, 4H), 6.06 (s, 1H), 2.73 (s, 3H), 2.68 (s, 3H), 2.65 (s, 3H), 2.58 (s, 3H), 1.53 (s, 3H), 1.48 (s, 3H), 1.44 (s, 3H), 1.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 191.5, 171.9, 160.3, 159.0, 157.5, 146.2, 145.7, 142.4, 135.4, 133.2, 131.8, 130.0, 129.6, 129.5, 127.9, 127.8, 121.8, 115.9, 115.8, 80.1, 79.1, 76.4, 76.1, 14.8, 14.3, 13.7, 13.3. MALDI-HRMS: calcd ([$C_{51}H_{40}B_2F_4N_4O$]$^+$) *m*/*z* = 822.3324, found *m*/*z* = 822.3253.

3.5. Synthesis of Compound C-1-L. Compound **C-1-L** was obtained following a procedure similar to that for compound **2**, except 2-thiopheneboronic acid (52.3 mg, 0.44 mmol) was used instead of 5-formyl-2-thiopheneboronic acid. A red solid was obtained (56.6 mg). Yield: 63.4%. Mp: 155.5–156.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 7.51–7.47 (m, 3H), 7.347–7.30 (m, 3H), 7.07 (t, 1H, *J* = 5.1 Hz), 6.84 (d, 1H, *J* = 3.4 Hz), 6.02 (s, 1H), 2.58 (s, 6H), 1.39 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 156.7, 154.3, 144.1, 142.3, 140.3, 135.2, 134.7, 132.1, 130.9, 129.4, 129.2, 128.1, 127.8, 127.3, 126.0, 121.9, 30.5, 14.9, 14.7, 13.5, 12.9. TOF HRMS ESI$^+$: calcd ([$C_{23}H_{21}BF_2N_2S$]$^+$) *m*/*z* = 406.1487, found *m*/*z* = 406.1498.

3.6. Synthesis of Compound C-2-L. Compound **C-2-L** was obtained following a procedure similar to that for compound **5**, except ethynylbenzene (13.0 mg, 0.12 mmol) was used instead of 4-ethynylbenzaldehyde. A blue solid was obtained (22.6 mg). Yield: 95.0%. Mp: >250 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 7.52–7.45 (m, 9H), 7.35 −7.26 (m, 6H), 6.05 (s, 1H), 2.72 (s, 3H), 2.67 (s, 3H), 2.65 (s, 3H), 2.58 (s, 3H), 1.51 (s, 3H), 1.47 (s, 3H), 1.44 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 160.1, 158.9, 157.4, 146.1, 145.5, 142.2, 135.2, 134.4, 134.1, 133.0, 131.7, 129.8, 129.6, 129.5, 129.3, 127.8, 127.7, 125.8, 121.6, 115.6, 86.2, 79.9, 78.9, 76.2, 75.9, 14.6, 14.1, 13.5, 13.2. MALDI-HRMS: calcd ($[C_{50}H_{40}B_2F_4N_4]^+$) m/z = 794.3375, found m/z = 794.3428.

3.7. Synthesis of Compound C-1. Under N_2 atmosphere, compound **2** (35.0 mg, 0.08 mmol) and sarcosine (24.0 mg, 0.27 mmol) were added to the solution of C_{60} (57.6 mg, 0.08 mmol) in toluene (50 mL). The mixture was heated to 110 °C, and the mixture was refluxed for 22 h and then cooled slowly to ambient temperature. The solvent was then removed under reduced pressure. The residue was purified by column chromatography (silica gel, toluene/hexane, 5:1, v/v). A red solid was obtained (32.5 mg). Yield: 34.4%. Mp: >250 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 7.47 (m, 3H), 7.35 (s, 1H), 7.26 (m, 2H), 6.74 (s, 1H), 6.01 (s, 1H), 5.25 (s, 1H), 4.99 (d, 1H, J = 9.0 Hz), 4.27 (d, 1H, J = 9.4 Hz), 2.95 (s, 3H), 2.57 (s, 3H), 2.51 (s, 3H), 1.37 (s, 3H), 1.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 156.9, 156.0, 154.1, 153.4, 153.1, 150.2, 147.5, 146.5, 146.3, 146.1, 145.7, 145.5, 144.9, 144.5, 144.3, 143.4, 142.8, 142.3, 142.1, 141.7, 140.3, 137.1, 135.1, 129.4, 129.3, 128.3, 128.1, 127.2, 122.0, 79.6, 70.1, 68.9, 40.6, 29.9, 14.7, 12.9. MALDI-HRMS calcd ($[C_{86}H_{26}BF_2N_3S]^-$) m/z = 1181.1909, found m/z = 1181.1980. Anal. Calcd for $C_{86}H_{26}BF_2N_3S$ + $0.5C_7H_8$ + 0.2DMF: C, 87.08; H, 2.57; N, 3.60. Found: C, 87.13; H, 2.75; N, 3.60.

3.8. Synthesis of Compound C-2. Compound **C-2** was obtained following a procedure similar to that for compound **C-1**, except compound **5** (30.0 mg, 0.036 mmol) was used instead of compound **2**. A blue solid was obtained (30.8 mg). Yield: 54.4%. Mp: >250 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 7.53−7.50 (m, 3H), 7.26 (m, 2H), 6.05 (s, 1H), 5.00 (d, 1H, J = 9.5 Hz), 4.93 (s, 1H), 4.27 (d, 1H, J = 9.2 Hz), 2.80 (s, 3H), 2.70 (s, 3H), 2.66 (s, 3H), 2.65 (s, 3H), 2.57 (s, 3H), 1.50 (s, 3H), 1.46 (s, 3H), 1.44 (s, 3H), 1.39 (s, 3H). MALDI-HRMS: calcd ($[C_{113}H_{45}N_5B_2F_4]^-$) m/z = 1569.3797, found m/z = 1569.3793. Anal. Calcd for $C_{113}H_{45}N_5B_2F_4$ + 0.25DMF: C, 86.01; H, 2.99; N, 4.62. Found: C, 86.02; H, 3.22; N, 4.62.

3.9. TTA Upconversion. A diode-pumped solid-state laser (532 and 589 nm, continues wave, CW) was used for the upconversions. The diameter of the laser spot was ca. 3 mm. For the upconversion experiments, the mixed solution of the fullerene dyads (triplet sensitizer) and perylene (triplet acceptor) was degassed for at least 15 min with N_2 or Ar, and the gas flow was maintained during the measurement. Then the solution was excited with a laser. The upconverted fluorescence of perylene was observed with a spectrofluorometer. In order to repress the scattered laser, a black box was put behind the fluorescent cuvette to trap the laser beam after it passed through the cuvette. The photographs of the upconversion were taken with a Samsung NV5 CCD digital camera. The exposure time of the photos is 1 s (the default value of the digital camera under the experimental conditions).

The upconversion quantum yields (Φ_{UC}) were determined with the prompt fluorescence of 2,6-diiodo-1,3,5,7-tetramethyl-8-phenyl-4,4-difluoroboradiazaindacene (**iodo-BDP**, structure shown in Scheme 1) (Φ = 2.7% in MeCN) and **BisBDPI** (structure shown in Scheme 1, Φ_F = 10.5% in toluene) as the standards. The upconversion quantum yields were calculated with eq 1, where Φ_{UC}, A_{unk}, I_{unk}, and η_{unk} represent the quantum yield, absorbance, integrated photoluminescence intensity, and the refractive index of the solvents (eq 1). The equation is multiplied by factor 2 in order to make the maximum quantum yield unity.[5a]

$$\Phi_{UC} = 2\Phi_{std}\left(\frac{A_{std}}{A_{unk}}\right)\left(\frac{I_{unk}}{I_{std}}\right)\left(\frac{\eta_{unk}}{\eta_{std}}\right)^2 \qquad (1)$$

For the measurement of the TTET efficiency, i.e., the Stern−Volmer quenching constants, the concentration of the sensitizer was fixed at 1.0 × 10^{-5} M, and the lifetime of the sensitizer was measured by LP920 with increasing perylene concentration in the solution.

The delayed fluorescence of the upconversion was measured with a nanosecond pulsed laser, Opolett 355II + UV nanosecond pulsed laser, typical pulse length: 7 ns. Pulse repetition: 20 Hz. Peak OPO energy: 4 mJ. The wavelength is tunable from 210 to 355 nm and from 420 to 2200 nm, which is synchronized to an FLS 920 spectrofluorometer. The pulsed laser was sufficient to sensitize the TTA upconversion. The decay kinetics of the upconverted fluorescence (delayed fluorescence) were monitored with an FLS920 spectrofluorometer (synchronized to the OPO nanosecond pulsed laser). The prompt fluorescence lifetime of the triplet acceptor perylene was measured with an EPL picoseconds pulsed laser (405 nm) which was synchronized to the FLS 920 spectrofluorometer.

3.10. DFT Calculations. The geometries of the compounds were optimized using density functional theory (DFT) with the B3LYP functional and 6-31G(d) basis set. There are no imaginary frequencies for all optimized structures. The spin density surfaces of the dyads were calculated at the B3LYP/6-31G(d) level. All calculations were performed with Gaussian 09W.[41]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, molecular structure characterization, additional spectra, and coordinates of the optimized geometries of **C-1** and **C-2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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