Journal of
Materials Chemistry

Cite this: *J. Mater. Chem.*, 2012, **22**, 20273

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**PAPER**

# Using $C_{60}$-bodipy dyads that show strong absorption of visible light and long-lived triplet excited states as organic triplet photosensitizers for triplet–triplet annihilation upconversion†

**Pei Yang, Wanhua Wu, Jianzhang Zhao,* Dandan Huang and Xiuyu Yi**

***Received 4th July 2012, Accepted 9th August 2012***
**DOI: 10.1039/c2jm34353c**

The synthesis of visible light-harvesting $C_{60}$-bodipy dyads (bodipy = boron-dipyrromethene), and the study of the photophysical properties and the application of dyads as heavy-atom free organic triplet photosensitizers for triplet–triplet annihilation (TTA) based upconversion, are reported. By attaching carbazole units to the π-core of the bodipy chromophore *via* an ethynyl linker, the absorption wavelength of the antenna in the dyads is readily tuned from 504 nm for the unsubstituted bodipy, to 538 nm (one carbazole unit, $\varepsilon = 61\,800\ \mathrm{M^{-1}\ cm^{-1}}$) and 597 nm (two carbazole units, $\varepsilon = 58\,200\ \mathrm{M^{-1}\ cm^{-1}}$). Upon photoexcitation at 538 nm (dyad **C-1**) or 597 nm (dyad **C-2**), intramolecular energy transfer from the antenna to the $C_{60}$ unit occurs, and as a result, the singlet excited state of the $C_{60}$ unit is populated. Subsequently, with the intrinsic intersystem crossing (ISC) of $C_{60}$, the triplet excited state of the $C_{60}$ unit is produced ($\tau_T$ up to 24.5 μs). Thus, without the need for any heavy atoms, the triplet excited state of the dyads was populated upon visible light excitation. The population of the $C_{60}$-localized triplet excited state of the dyads was confirmed by nanosecond time-resolved transient difference absorption spectra and spin density analysis. The dyads were used as triplet photosensitizers for TTA upconversion and upconversion quantum yields of up to 2.9% were observed.

## Introduction

Triplet photosensitizers have attracted much attention, due to their applications in photodynamic therapy (PDT),[1–3] photocatalysis,[4–8] and more recently, triplet–triplet annihilation (TTA) based upconversions.[9–15] The typical triplet photosensitizers for TTA upconversions are Pt(II) porphyrin complexes, and Ru(II) or Ir(III) complexes.[11–13] In these complexes, the heavy atom effect of the transition metal atoms facilitates the intersystem crossing (ISC), thus the triplet excited state can be populated upon photoexcitation.[16] However, these complexes usually show relatively weak absorption in the visible range ($\varepsilon$ value is smaller compared to typical chromophores such as rhodamine, fluorescein, *etc.*).[17–20] Recently iodo- and bromo-bodipy (bodipy = boron dipyrromethane) have been devised as triplet photosensitizers for sensitizing singlet oxygen ($^1O_2$) and TTA based upconversion.[2a,21,22] These photosensitizers show strong absorption in the visible range, which is a desired property for triplet photosensitizers. However, all these triplet photosensitizers required the heavy atom effect of Pt(II), Ir(III) or iodine, *etc.* As a result, these compounds are generally not cost-efficient and in some circumstances the derivatization of the compounds, while retaining the ISC property, is difficult. From the point of view of photochemistry, it is highly desirable to develop heavy-atom free organic triplet photosensitizers, especially those with variable structures and predictable ISC properties. However, it is still a substantial challenge to design an organic chromophore without any heavy atoms which possesses the predetermined ISC property.[16a] Porphyrins and some perylenebisimides are such organic triplet photosensitizers,[1,23] but it is clear that the molecular diversity of this class of heavy-atom free organic triplet photosensitizers needs to be increased.

Similar challenges exist for TTA upconversion, which has attracted much attention due to its potential application in photovoltaics, luminescent bioimaging, photocatalysis and oxygen sensing.[11–13,24] TTA upconversion shows some advantages over the conventional upconversion methods, such as those with rare earth metal materials,[25] and two-photon absorption dyes.[26] Currently, most of the triplet photosensitizers are Pt(II) porphyrin complexes, Pt(II) complexes, and Ir(III) acetylide complexes, *etc.*[12] Organic triplet photosensitizers for TTA upconversion are rarely reported,[22,24c,27,28] and the development of heavy-atom free organic triplet photosensitizers is highly desired.[12] To date this is still a major challenge in photochemistry.[16a]

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*State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, E-208 Western Campus, 2 Ling-Gong Road, Dalian 116024, P. R. China. E-mail: zhaojzh@dlut.edu.cn; Web: http://finechem.dlut.edu.cn/photochem; Fax: +86 411 84986236; Tel: +86 0411 84986236*

† Electronic supplementary information (ESI) available: $^1H$ and $^{13}C$ NMR, and MS spectra. Absorption and emission spectra, upconversion and DFT calculation details. See DOI: 10.1039/c2jm34353c

In order to address the above challenges, herein we propose a general molecular structure motif for organic triplet photosensitizers, *i.e.* the $C_{60}$-organic chromophore dyads.[29–48] The triplet excited states of the $C_{60}$ dyads are populated upon photooxidation without any heavy atoms in these compounds, despite complicated mechanisms which may involve direct ISC or charge separation and recombination, *etc.*[49–52] The molecular design rationale lies in the notion that fullerene $C_{60}$ shows efficient ISC, that is, the triplet excited state of $C_{60}$ is efficiently populated upon photoexcitation.[53] Therefore the fluorescence quantum yield of $C_{60}$ is very low ($\Phi_F < 0.1\%$). However, $C_{60}$ itself is not an ideal triplet photosensitizer because its absorption in the visible range is very weak, for example, $\varepsilon$ is 820 $M^{-1}$ $cm^{-1}$ at 530 nm.[49] This weak absorption is due to the symmetry forbidden transitions of $C_{60}$ ($S_0 \rightarrow S_1$, *etc.*).[53a] However, the low-lying $S_1$ state of $C_{60}$ ensures an intramolecular energy transfer from the light-harvesting antenna to the $C_{60}$ unit in a dyad.[30,33] Upon photoexcitation, the antenna is excited, and so an intramolecular energy transfer occurs from the antenna to the $C_{60}$ unit. As a result, the $S_1$ state of $C_{60}$ will be populated (energy level is 1.72 eV). Due to the efficient intrinsic ISC property of $C_{60}$, the triplet excited state of the $C_{60}$ will be populated. Thus, a triplet excited state will be produced upon photoexcitation in the visible range of the spectrum.

$C_{60}$-organic chromophore dyads have been used for photovoltaics,[47] and to improve the optical limiting property of $C_{60}$, *etc.*[30,33,39,43,54–57] Previously, a $C_{60}$ containing water-soluble polymer was studied for its PDT effect, but the polymer only gave weak absorption of visible light.[55a] Ru(II) and Re(I)-containing methanofullerenes were also studied, and the production of singlet oxygen ($^1O_2$) was observed.[55b] Improved optical limiting was observed for a $C_{60}$ derivative bearing a star-shaped multi-photon absorption chromophore.[55c] Very recently we reported the application of a visible light-harvesting $C_{60}$ for photooxidation.[5] Recently we also reported the first application of a $C_{60}$ dyad as a triplet photosensitizer for TTA upconversion,[58] but it is clear that the molecular structures of these new triplet photosensitizers need to be further explored in order to study the relationship between the molecular structure and the property of the dyads.

Bodipy was selected as the light-harvesting antenna due to its strong absorption of visible light and versatile derivatization chemistry.[59–62] Herein we attached carbazole units to the bodipy core. Thus, the absorption can be readily tuned from 504 nm for the unsubstituted bodipy, to 538 nm (dyad **C-1**) or 597 nm (dyad **C-2**). Carbazole is a versatile chromophore that is widely used in fluorophores or phosphores.[63] The two dyads are used as triplet photosensitizers for TTA upconversion, and an upconversion quantum yield of up to 2.9% was observed.

## Results and discussion

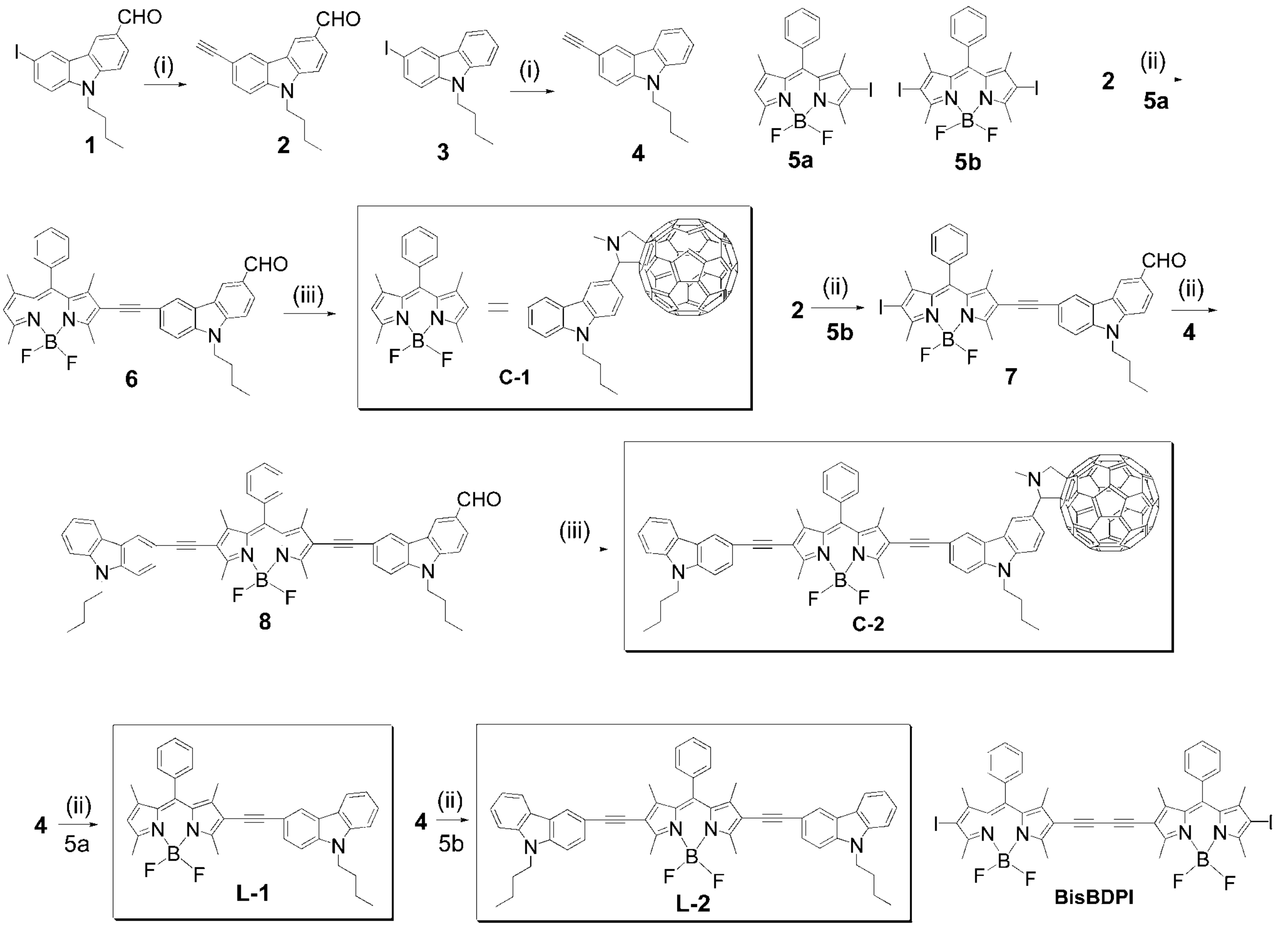
### Design and synthesis

The basic strategy of our molecular design rationale is to use bodipy as the core of the light-harvesting antenna. Bodipy is well-known for its strong absorption in the visible range (unsubstituted bodipy gives strong absorption at *ca.* 504 nm, $\varepsilon$ = 80 000 $M^{-1}$ $cm^{-1}$).[59–66] The absorption wavelength is easily extended to the red range by extension of the π-conjugation framework by attaching carbazole to the bodipy core *via* an ethynyl bond (–C≡C–), to ensure efficient electronic communication.[22,66] Previously, (bodipy)$_3$–porphyrin–$C_{60}$ pentad was studied.[39] A flexible linker was used between the bodipy antenna and $C_{60}$.[39] Herein, a rigid linker was used for **C-1** and **C-2** (Scheme 1). The preparation of the light-harvesting antenna is based on the rich derivatization of the carbazole and bodipy moieties. The ethynyl bonds were introduced by the Pd(0) catalyzed Sonogashira coupling. Formyl groups were attached to the carbazole by the Vilsmeier–Haack reaction. Confalone reaction,[67] or 1,3-dipolar cycloaddition of azomethine ylides of the $C_{60}$, sarcosine and the functionalized carbazole-bodipy leads to the $C_{60}$-bodipy dyads. All the compounds were prepared in moderate to good yields. Control compounds **L-1** and **L-2** were also prepared for the photophysical studies. The molecular structures of the compounds were fully confirmed by $^1H$ NMR, $^{13}C$ NMR, and high resolution mass spectrometry (HR MS). We noted the broadening signal of the $^1H$ NMR spectra, which may be due to the restricted rotation of the antennas attached to the $C_{60}$ unit (ESI†).[68] Previously, styryl-bodipy-$C_{60}$ dyads were reported.[69] Herein we used the acetylene bond as the π-conjugating linker.

### Steady-state electronic spectroscopy (absorption and emission)

Firstly the UV-vis absorption of the compounds were studied (Fig. 1). $C_{60}$ gives very weak absorption in the visible range. The absorption maximum is located at 335 nm ($\varepsilon$ = 59 400 $M^{-1}$ $cm^{-1}$). The antenna **L-1** gives strong absorption at 539 nm ($\varepsilon$ = 51 700 $M^{-1}$ $cm^{-1}$). Interestingly, **C-1** gives a similarly strong absorption at 538 nm ($\varepsilon$ = 61 800 $M^{-1}$ $cm^{-1}$) (Fig. 1). With two carbazole units connected to the bodipy core, antenna **L-2** gives a red-shifted absorption at 599 nm ($\varepsilon$ = 65 500 $M^{-1}$ $cm^{-1}$). Accordingly, the dyad **C-2** gives a similarly strong absorption at 597 nm ($\varepsilon$ = 58 200 $M^{-1}$ $cm^{-1}$). The absorptions of the dyads are roughly the sum of the absorption of $C_{60}$ and the antenna. Thus, the electronic interaction of the antenna and $C_{60}$ unit is weak at the ground state.[33,45] It should be noted that the dyads show intense absorption in the visible range, which is beneficial for potential applications. The absorption of the dyads are slightly red-shifted compared to the bodipy-$C_{60}$ dyads containing no electron-donating carbazole moieties.[58] The absorption of **C-1** and **C-2** are red-shifted compared to a similar $C_{60}$-bodipy dyad.[33]

In order to confirm the intramolecular energy transfer, the fluorescence of the dyads were studied (Fig. 2). $C_{60}$ gives a very weak emission upon excitation at 530 nm, due to its weak absorption at 530 nm ($\varepsilon$ = 820 $M^{-1}$ $cm^{-1}$) and low fluorescence quantum yield ($\Phi_F < 0.1\%$). **L-1** gives an emission at 609 nm ($\Phi_F = 3.9\%$). Thus, the $S_1$ state energy level of **L-1** (2.04 eV) is higher than the $S_1$ state energy level of $C_{60}$ (1.72 eV), and the intramolecular energy transfer from the antenna to $C_{60}$ unit is possible. The fluorescence of **C-1** is very weak, that is, the emission of the antenna is completely quenched. Thus, we propose that efficient intramolecular energy transfer occurs for dyad **C-1** upon photoexcitation. The energy transfer efficiency was calculated as 97.4% based on the quenched fluorescence. The energy transfer is supported by the enhanced fluorescence emission of the $C_{60}$ unit in the dyads (Fig. 2a inset).[34,37,45,69,70]



**Scheme 1** Synthesis of the $C_{60}$-bodipy dyads **C-1** and **C-2**. The molecular structures of the control compounds **L-1** and **L-2** as the light-harvesting antenna in **C-1** and **C-2**, as well as the standard for measurement of upconversion quantum yields are also included. (i) $PdCl_2(PPh_3)_2$, $PPh_3$, CuI, $NEt_3$, ethynyltrimethylsilane, argon atmosphere, 80 °C, 4 h; then $K_2CO_3$, r.t. 6 h; (ii) $PdCl_2(PPh_3)_2$, $PPh_3$, CuI, $NEt_3$, THF, argon atmosphere, 60 °C, 6 h; (iii) sarcosine, $C_{60}$, toluene, reflux.

Similar emission profiles were observed for dyad **C-2** and the components (Fig. 2b). For example, the antenna **L-2** shows an intense emission at 648 nm, but the emission was completely quenched in the dyad **C-2**. Similar to **C-1**, fluorescence of $C_{60}$ was observed for **C-2**, due to the light-harvesting effect of the antenna. The intramolecular energy transfer efficiency was estimated as 97.7% based on the quenched emission of antenna in **C-2**. It should be pointed out that the intramolecular charge transfer from the antenna to $C_{60}$ unit cannot be excluded.[33,69,71]

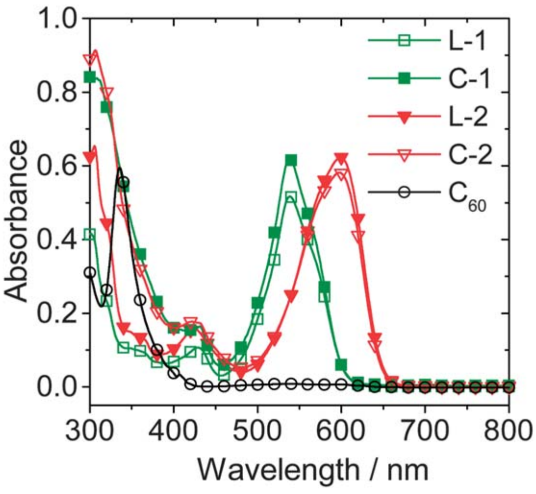


**Fig. 1** UV-vis absorption spectra of the $C_{60}$-bodipy dyads **C-1** and **C-2**, and the light-harvesting antenna of the dyads; $c = 1.0 \times 10^{-5}$ M in toluene, 20 °C.

## Electrochemistry

The redox potentials of the antennas and the dyads were studied (Table 1 and ESI†).[71] The first oxidation (bodipy moiety) and the first reduction ($C_{60}$ moiety) of the dyad **C-1** are 0.78 and −1.27 V, respectively. Thus, the driving force for the charge recombination process of the charge separated state of the dyad **C-1** was determined as 2.06 eV. The driving force for the charge-separation process ($-\Delta G_{CS}$, with bodipy as the electron donor and $C_{60}$ as the electron acceptor) of **C-1** was calculated as 0.01 eV. Similarly, the $-\Delta G_{CS}$ value of **C-2** was estimated as 0.20 eV. Therefore, the photo-induced charge separation is thermodynamically allowed.[71] Our later study indicated that the triplet excited state of the dyads was populated, which is either due to the direct energy transfer/ISC or the

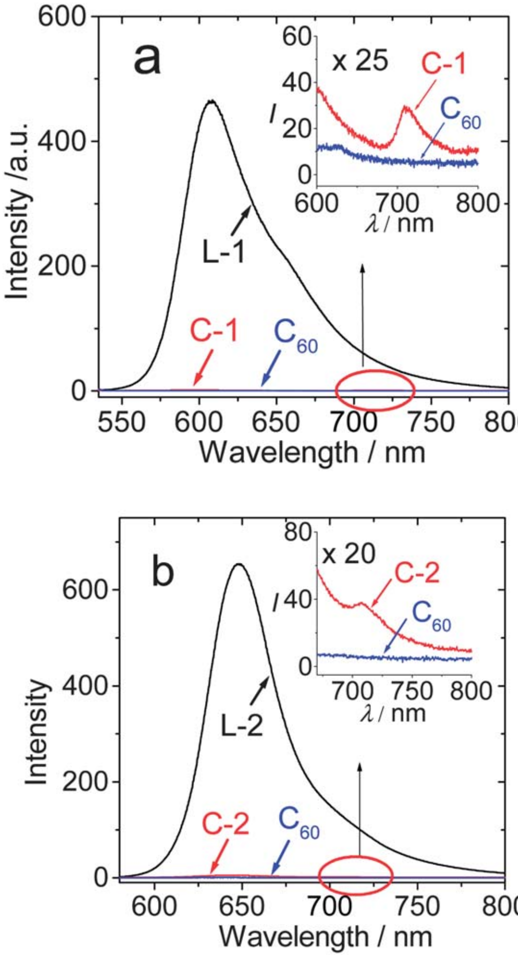


**Fig. 2** (a) Emission spectra of **L-1**, **C-1** and $C_{60}$, $\lambda_{ex}$ = 530 nm. (b) Emission spectra of **L-2**, **C-2** and $C_{60}$, $\lambda_{ex}$ = 570 nm. In toluene, $1.0 \times 10^{-5}$ M, 20 °C.

**Table 1** Electrochemical data of **L-1**, **L-2**, **C-1** and **C-2**[a]

| | Oxidation | | Reduction | |
|---|---|---|---|---|
| | $E_1{}^b$/V | $E_2{}^c$/V | $E_1{}^b$/V | $E_2{}^c$/V |
| **L-1**[d] | +0.61 | +1.21 | −1.45 | — |
| **C-1**[e] | +0.78 | +1.32 | −1.27 | −1.54 |
| **L-2**[e] | +0.79 | +1.16 | −1.48 | — |
| **C-2**[e] | +0.76 | +1.32 | −1.11 | −1.51 |

[a] Determined by a Pt working electrode in deaerated $CH_2Cl_2$ + 0.1 M *n*-$Bu_4NBF_4$ at room temperature. CVs were obtained using a scan rate of 50 mV $s^{-1}$ and a step potential of 1 mV. Values of potentials ($E$) for all compounds *versus* silver–silver chloride electrode. [b] One electron process. [c] Bielectronic process. [d] In solution. [e] Solid film on glassy carbon working electrode.

charge recombination.[33,69] Previously it was proposed that the singlet–singlet energy transfer from the antenna is ultra-fast as is often observed in such dyads.[71a] Upon population of the fullerene singlet, the electron transfer is then not allowed thermodynamically, thus, direct population of the triplet state by intramolecular energy transfer and ISC of $C_{60}$ is also possible.[71a]

### Nanosecond time-resolved transient difference absorption spectroscopy

The intramolecular energy transfer from the antenna to the $C_{60}$ unit will produce the singlet excited state of $C_{60}$. In turn, the triplet excited state of $C_{60}$ unit will be populated *via* the ISC of $C_{60}$. In order to confirm the triplet excited states upon photoexcitation, nanosecond time-resolved transient difference absorption spectroscopy of the compounds was carried out (Fig. 3).[45,69]

Upon pulsed laser excitation of **C-1** at 532 nm, at which the absorption is mainly assigned to the antenna part, and the absorption of $C_{60}$ unit can be neglected, transience at 367 and 700 nm was observed (Fig. 3a), which are the characteristic absorptions of the triplet excited state of $C_{60}$.[33] Interestingly, the bleach of the ground state absorption of the antenna at 538 nm was not observed, indicating that the $T_1$ state is exclusively localized on $C_{60}$ unit. (Fig. 3a). The lifetime of the transient was determined as 20.2 μs (in deaerated solution), which was significantly reduced to 0.3 μs in aerated solution. The production of singlet oxygen ($^1O_2$) in aerated solution with the **C-1** was confirmed by photooxidation of 1,5-dihydroxylnaphthelene (see ESI†, Fig. S21). These results indicated that the transience observed in the time-resolved absorption spectra is due to the $C_{60}$-localized triplet excited state, and that the charge separated state is not significant.[69,72]

Similar transience was observed for **C-2** (Fig. 3c). The lifetime of the $C_{60}$-localized triplet state of **C-2** was determined as 24.5 μs, which was reduced to 0.35 μs in aerated solution. The photophysical properties of the antenna and the dyads were summarized in Table 2. We noted that the triplet excited state lifetimes of **C-1** and **C-2** are slightly shorter than the recently reported $C_{60}$-bodipy dyads.[58] Previously it was found that the triplet state is delocalized over bodipy antenna and $C_{60}$ part in a $C_{60}$-bodipy dyad.[33] For **C-1** and **C-2**, however, the triplet state is exclusively

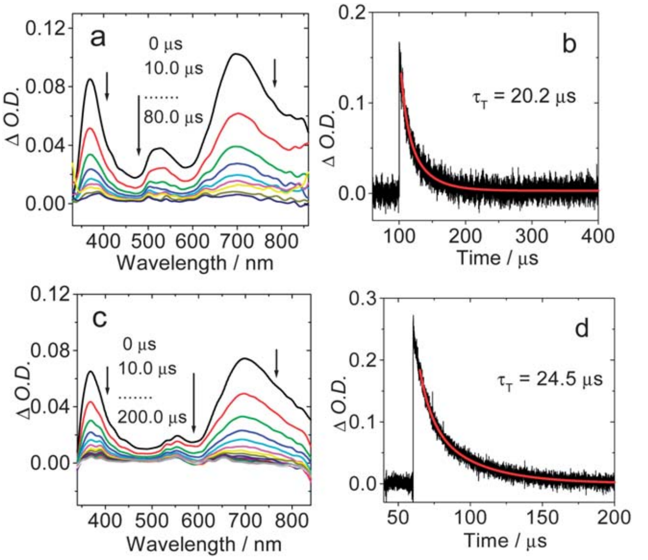


**Fig. 3** Nanosecond time-resolved transient difference absorption spectra of (a) **C-1** ($\lambda_{ex}$ = 532 nm) and (c) **C-2** ($\lambda_{ex}$ = 532 nm); decay traces of the transience of (b) **C-1** at 700 nm, and (d) **C-2** at 700 nm. In deaerated toluene, $1.0 \times 10^{-5}$ mol $dm^{-3}$, 20 °C.

**Table 2** Photophysical parameters of the $C_{60}$ dyads and the components[a]

| | $\lambda_{abs}$ (nm) | $\lambda_{em}$ (nm) | $\varepsilon$ ($M^{-1}$ $cm^{-1}$)[b] | $\Phi_F$[c] | $\tau$ |
|---|---|---|---|---|---|
| $C_{60}$ | 335 | — | 59 400 | — | 18.6 μs[d] |
| **L-1** | 539 | 609 | 51 700 | 3.9% | 1.8 ns[e] |
| **L-2** | 599 | 648 | 65 500 | 13.1% | 2.2 ns[e] |
| **C-1** | 538 | 598 | 61 800 | 0.1% | 20.2 μs[d] |
| **C-2** | 597 | 642 | 58 200 | 0.3% | 24.5 μs[d] |

[a] In toluene ($1.0 \times 10^{-5}$ mol $dm^{-3}$). [b] Molar extinction coefficient at the absorption maxima. [c] With 4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene (Bodipy) as the standard ($\Phi$ = 72.0% in THF). [d] Triplet state lifetimes, measured by transient absorptions. [e] Fluorescence lifetimes.

localized on $C_{60}$. Note the UV-vis absorption of **C-2** is red-shifted compared to **C-1**. However, the $T_1$ state of **C-2** is still localized on $C_{60}$, which means the $T_1$ state energy level of the antenna in **C-2** is not decreased. This result is different from a $C_{60}$-bodipy dyad which shows a similar absorption wavelength but for which the $T_1$ state is localized on the styryl-bodipy part.[69] $C_{60}$ dyads with red-shifted absorptions but high $T_1$ state energy levels are beneficial for applications based on TTET process.

## Spin density analysis of the dyads

In order to confirm the localization of the triplet excited states of the dyads from a theoretical perspective, the spin density surfaces of the triplet state of the dyads were calculated by density functional theory (DFT. Fig. 4).[5,58] For dyad **C-1**, the spin density is localized on the $C_{60}$ unit and the antenna makes no contribution. Thus, the spin density of **C-1** confirms that the triplet excited state of dyad **C-1** is localized on $C_{60}$. A similar result was obtained for dyad **C-2**, for which the spin density surface is localized on the $C_{60}$ unit. These results are in full agreement with the time-resolved transient absorption spectra of the dyads (Fig. 3).

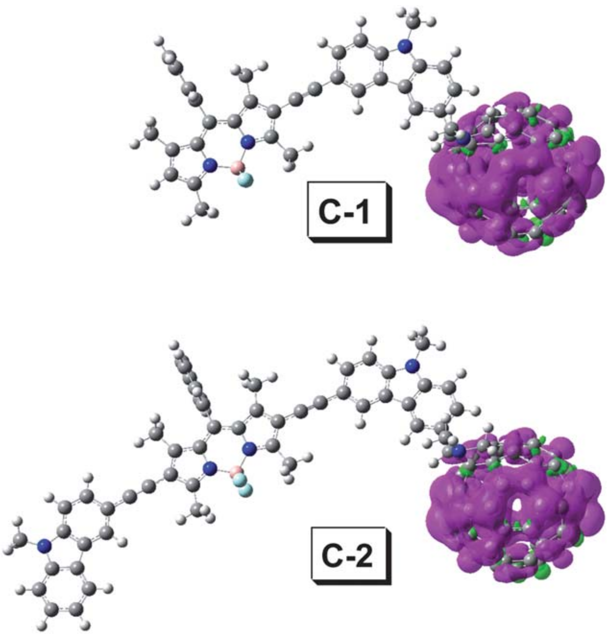


**Fig. 4** Spin-density surface of **C-1** and **C-2** at the optimized triplet state geometry. Toluene was used as solvent in the calculations. Calculated at B3LYP/6-31G(d) level with Gaussian 09W.

## $C_{60}$-bodipy dyads as the organic triplet photosensitizer for the TTA upconversion

$C_{60}$ dyad **C-1** and dyad **C-2** show strong absorptions of visible light and long-lived triplet excited states, and as a consequence, they are suitable to be used as triplet photosensitizers for TTA upconversion.[11–13] Thus, the use of the dyads in TTA upconversion was studied (Fig. 5). Previously, $C_{60}$ dyads with strong visible light absorption or panchromatic absorption were prepared,[33,35,39,44,69,73] but very few visible light-harvesting $C_{60}$ dyads were used for sensitizing a photophysical process.[36,74] Aza-bodipy-$C_{60}$ dyad was reported recently, and the population of the triplet excited of the aza-bodipy antenna was proposed.[45] However, the dyad was not employed for sensitizing a photophysical process. The triplet excited states of bodipy-$C_{60}$ dyads were also studied.[33] Very recently we used $C_{60}$-bodipy dyads as triplet photosensitizers,[58] but much room is left for the application of the triplet excited states of $C_{60}$-organic chromophore dyads.

Upon excitation with a 532 nm laser (Fig. 5a), **C-1** gives weak emissions at 598 and 712 nm, which are due to the emission of the antenna and $C_{60}$ unit, respectively. With addition of perylene (triplet acceptor/emitter), an intense emission in the 430–530 nm range was observed. Irradiation of perylene alone with the 532 nm laser did not produce this emission band, thus confirming the upconversion feature of the blue emission. The upconversion quantum yield ($\Phi_{UC}$) was determined as 2.3%. Similar results were observed for **C-2**, and a $\Phi_{UC}$ of 2.9% was observed (Fig. 5b and Table 3). To the best of our knowledge, this is the first time that TTA upconversion has been carried out with organic triplet photosensitizers (heavy atom-free) that show absorption in the red range.[11,12,24c,58] We envisage that a great amount of organic triplet photosensitizers can be developed following our strategy of using $C_{60}$-organic chromophore dyads. We noted that the upconversion quantum yields with **C-1** and **C-2** as triplet photosensitizers are lower than the recently reported $C_{60}$ dyad triplet photosensitizers for TTA upconversion.[58] The lower

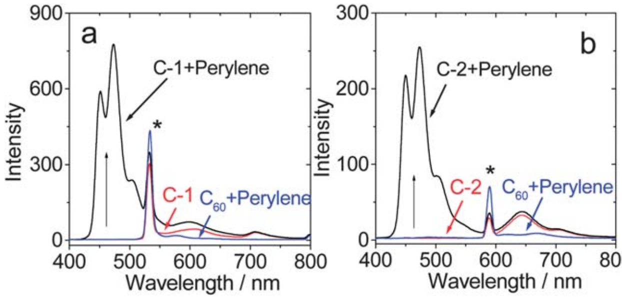


**Fig. 5** TTA upconversion with (a) **C-1** ($\lambda_{ex}$ = 532 nm, laser) and (b) **C-2** ($\lambda_{ex}$ = 589 nm, laser) as the triplet photosensitizers and perylene as the acceptor. The asterisks in (a) and (b) indicate the scattered laser. In toluene: *c* (dyads) = $5.0 \times 10^{-6}$ M, *c* (perylene) = $3.0 \times 10^{-4}$ M, 20 °C. Excited with CW lasers (5 mW).

**Table 3** Triplet excited state lifetimes ($\tau_T$), Stern–Volmer quenching constants ($K_{SV}$), and bimolecular quenching constants ($k_q$) of the chromophore/$C_{60}$ dyads as organic sensitizers. Perylene was used as the quencher. In deaerated toluene solution, 20 °C

| | $\tau_T$ (μs) | $K_{sv}$ ($10^3$ $M^{-1}$) | $k_q$ ($10^9$ $M^{-1}$ $s^{-1}$) | $\Phi_{UC}$ (%) |
|---|---|---|---|---|
| $C_{60}$ | 18.6 | 28.1 | 1.51 | — |
| **C-1** | 20.2 | 4.9 | 0.24 | 2.3[a] |
| **C-2** | 24.5 | 8.2 | 0.33 | 2.9[b] |

[a] Excited with 532 nm laser, with the prompt fluorescence of 2,6-diiodo-BDP (**5b**) as the standard ($\Phi_F = 2.7\%$ in MeCN). [b] Excited with 589 nm laser, with the prompt fluorescence of **BisBDPI** as the standard ($\Phi_F = 10.5\%$ in toluene).

upconversion quantum yields with **C-1** and **C-2** may be due to the non-efficient production of the triplet excited state of the dyads upon photooxidation, *e.g.* caused by the intramolecular charge transfer.[33,69,71a]

For the TTA upconversions (Fig. 5), the fluorescence of the dyads are not quenched. This is reasonable because the triplet excited states, not the singlet excited states, were involved in the triplet–triplet energy-transfer process (Scheme 2).[11,12]

The upconversion is visible to un-aided eyes (Fig. 6). Dyad **C-1** gives a yellow-brown emission with 532 nm excitation (Fig. 6a). Upon addition of perylene (triplet acceptor), the emission color turns to blue, which is due to the upconversion. However, for $C_{60}$ alone, no blue emission was observed, this is due to the weak absorption of $C_{60}$ at 532 nm, despite of the ISC ability of $C_{60}$. The green color in Fig. 6a is due to the scattered excitation laser. For dyad **C-1**, the absorption at 532 nm is strong ($\varepsilon = 58\,400$ $M^{-1}$ $cm^{-1}$), thus the upconversion emission intensity is strong.

A similar result was observed for **C-2** (Fig. 6b). **C-2** gives a brown-red emission upon laser excitation at 589 nm. With the addition of perylene, an intense blue emission was observed. For the $C_{60}$-perylene mixture, no blue emission was observed.

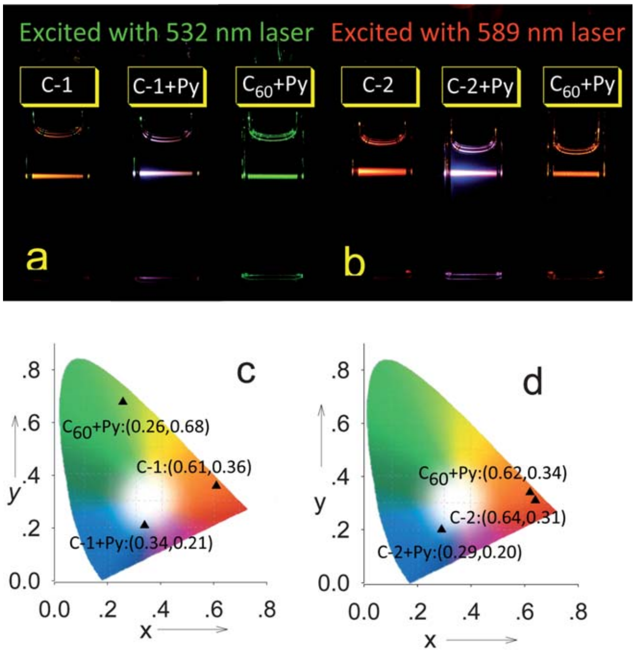
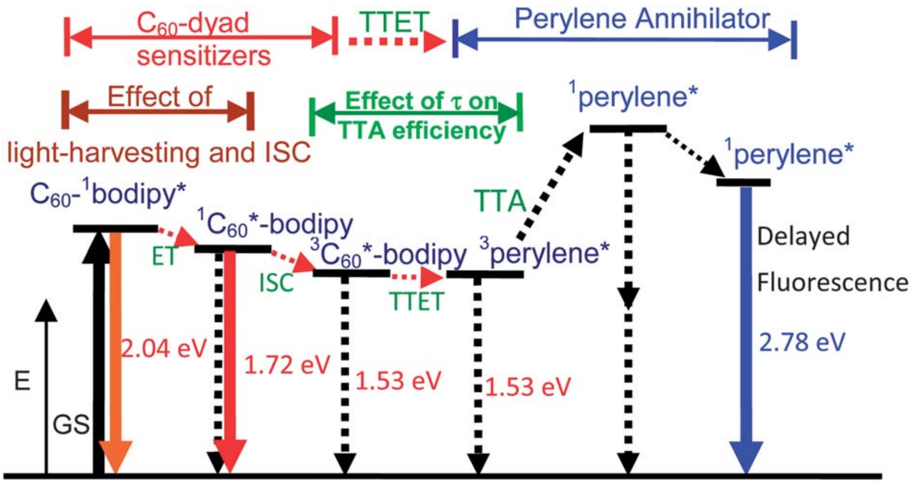


**Fig. 6** Photographs (a and b) of the emissions of triplet photosensitizers alone and the upconversion. Corresponding CIE diagrams (c and d) of the emission of sensitizers alone and in the presence of perylene (upconversion). In toluene; excited with CW lasers, 5 mW, *c* (dyads) = 5.0 × $10^{-6}$ M, *c* (perylene) = 3.0 × $10^{-4}$ M, 20 °C.

In order to confirm that the blue emission is due to the upconverted fluorescence, the luminescence lifetime of the blue emission was measured (Fig. 7). The luminescence lifetime of the upconversion with **C-1**/perylene was determined as 102.0 μs, which is the delayed fluorescence ($\tau_{DF}$) of the TTA upconversion.[75] The prompt fluorescence lifetime ($\tau_{PF}$) of perylene was determined as 4.2 ns. The long lifetime of the upconverted emission confirmed the delayed fluorescence feature of the



**Scheme 2** Jablonski diagram of triplet–triplet annihilation (TTA) upconversion with $C_{60}$-bodipy dyad **C-1** as triplet photosensitizer. $C_{60}$-$^1$bodipy* is the singlet excited state of **C-1** localized on bodipy unit. ET stands for energy-transfer. $^1C_{60}$*-bodipy is the singlet excited state of **C-1** localized on $C_{60}$ unit. $^3C_{60}$-bodipy* is the triplet excited state of **C-1** localized on bodipy unit. $^3C_{60}$*-bodipy is the triplet excited state of **C-1** localized on $C_{60}$ unit. TTET stands for triplet–triplet energy-transfer. $^3$perylene* is the triplet excited state of perylene. $^1$perylene* is the singlet excited state of perylene. The emission bands observed in the TTA experiment are the simultaneous $C_{60}$-$^1$bodipy* emission (fluorescence) and $^1$perylene* emission (delayed fluorescence). The triplet states of sensitizers and acceptors are non-emissive.

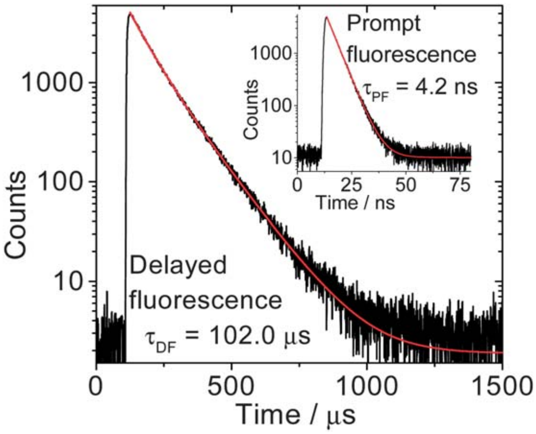


**Fig. 7** Delayed fluorescence in the TTA upconversion with **C-1** as triplet photosensitizer and perylene as the triplet acceptor. Excited at 532 nm (nanosecond pulsed OPO laser, synchronized with spectrofluorometer), the decay trace was monitored at 470 nm. Under such conditions, **C-1** was selectively excited and the emission is due to the upconverted emission of perylene. The inset shows the prompt fluorescence decay of perylene determined in a different experiment (excited with a 405 nm picosecond laser, the decay of the emission was monitored at 470 nm). In deaerated toluene. *c* (**C-1**) = $5.0 \times 10^{-6}$ M; *c* (perylene) = $3.0 \times 10^{-4}$ M, 20 °C.

emission observed in Fig. 5, thus, the blue emission for dyads/perylene mixed solution is due to the TTA upconversion. A similar result was observed for **C-2** ($\tau_{DF}$ = 63.0 µs, see ESI†).

In order to study the TTET efficiency, the quenching of the triplet excited states of **C-1** and **C-2** with perylene as the triplet quencher was studied (Fig. 8). The quenching constants were determined as $4.9 \times 10^3$ and $8.2 \times 10^3$ $M^{-1}$ for **C-1** and **C-2**, respectively. Higher quenching constants were observed for $C_{60}$ ($K_{sv} = 2.8 \times 10^4$ $M^{-1}$). It is worth noting that the triplet excited state lifetime of $C_{60}$ is slightly shorter than those of dyads **C-1** and **C-2**. The smaller molecular size of $C_{60}$ makes it diffuse more easily than the dyads. These results indicate that organic triplet photosensitizers with small molecular sizes will be better candidates for TTA upconversion.

The photophysics of the TTA upconversion with the dyads as triplet photosensitizers can be summarized in Scheme 2.[11–13] Upon excitation of the antenna of the dyads, the singlet excited state of the antenna is populated. Consequently, singlet excited state energy transfer from the antenna to the $C_{60}$ unit occurs. As a result, the singlet excited state of $C_{60}$ is populated, and in turn, the triplet excited state of $C_{60}$ is produced by the intrinsic ISC property of $C_{60}$. The triplet excited state of the dyad is localized on the $C_{60}$ unit. The excited state energy will be transferred from the $C_{60}$ unit to the triplet acceptor perylene by the TTET between the triplet excited state of the triplet photosensitizer and the triplet acceptor. Annihilation of the two acceptor molecules at the triplet excited state will produce a singlet excited state acceptor. Radiative decay from the singlet excited state gives the upconverted fluorescence emission, *i.e.* the delayed fluorescence.

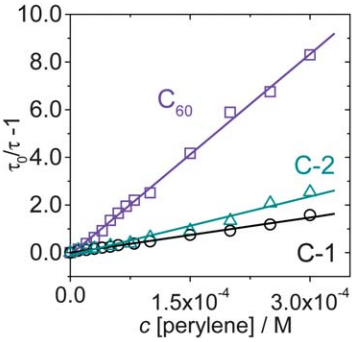


**Fig. 8** Stern–Volmer plots generated from the triplet excited state lifetime ($\tau_T$) quenching curves of the compounds measured as a function of perylene concentration. In toluene, 20 °C.

## Conclusions

In conclusion, $C_{60}$-bodipy dyads were prepared as organic triplet photosensitizers and were used for triplet–triplet annihilation based upconversion. The antenna in the dyads can be photoexcited by green and red light. Thereafter, the intramolecular singlet excited state energy transfer from antenna to $C_{60}$ unit produces the singlet excited state of $C_{60}$. The intrinsic intersystem crossing of $C_{60}$ produces the triplet excited states of the $C_{60}$ unit. Therefore, without any heavy atoms, the triplet excited state of the dyads can be populated upon photoexcitation. The absorption of the dyads was readily tuned by attaching different carbazole moieties to the π-core of bodipy *via* ethynyl bonds. The population of the $C_{60}$-localized triplet excited state of the dyads upon photoexcitation was confirmed by nanosecond time-resolved transient absorption spectroscopy and spin density surface analysis. The dyads were used as triplet photosensitizers for TTA upconversion and upconversion quantum yields of up to 2.9% were observed. We propose that $C_{60}$-organic chromophore dyads can be used as general molecular structural motifs for heavy-atom free organic triplet photosensitizers, with potential applications in photovoltaics, photocatalysis, photodynamic therapy, and TTA upconversion.

## Experimental

Fluorescence lifetimes of the compounds were measured with a OB920 phosphorescence/fluorescence lifetime spectrometer (Edinburgh Instruments, UK). Nanosecond time-resolved transient difference absorption spectra were measured on a LP920 laser flash photolysis spectrometer (Edinburgh Instruments, UK). The transient data were recorded on a Tektronix TDS 3012B oscilloscope. The lifetime values (by monitoring the decay trace of the transients) were obtained with LP900 software. Compounds **1** and **3**,[76] **5a**,[22] and **5b**,[65] were prepared according to the respective literature.

### Compound 2

Under Ar atmosphere, compound **1** (190.0 mg, 0.50 mmol), $PdCl_2(PPh_3)_2$ (10.6 mg, 0.015 mmol), $PPh_3$ (6.6 mg, 0.025 mmol) and CuI (4.8 mg 0.025 mmol) were dissolved in triethylamine (12 mL). After stirring, ethynyltrimethylsilane (0.3 mL, 2.95 mmol) was added *via* syringe. The solution was stirred at 80 °C for 4 h. After removal of solvent under reduced pressure, the residue was purified with column chromatography (silica gel; dichloromethane/petroleum ether (30–60 °C) = 3 : 1, v/v) to give a colourless oil. Then, a mixture of the resultant product, $K_2CO_3$ (1.6 g 1.2 mmol), $CH_2Cl_2$ (4 mL) and $CH_3OH$ (8 mL) was stirred at rt for 6 h to remove the trimethylsilane group. The solution was washed with water and the aqueous phase was extracted with $CH_2Cl_2$. After removal of solvent under reduced pressure, the residue was purified by column chromatography (silica gel, $CH_2Cl_2$/petroleum ether (30–60 °C) = 3 : 1 v/v) to give 120.0 mg of **1** as a yellow powder. Yield: 87%; m.p. = 116.4–117.8 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 10.08 (s, 1H), 8.53 (s, 1H), 8.27 (s, 1H), 8.02 (d, 1H, $J$ = 8.6 Hz), 7.64 (d, 1H, $J$ = 8.4 Hz), 7.46 (d, 1H, $J$ = 8.6 Hz), 7.38 (d, 1H, $J$ = 8.4 Hz), 4.32–4.28 (t, 2H, 7.2 Hz), 3.10 (s, 1H), 1.88–1.81 (m, 2H), 1.41–1.35 (m 2H), 0.96–0.93 (t, 3H, 7.4 Hz); TOF HRMS EI+: $C_{19}H_{17}NO^+$, calculated $m/z$ = 275.1310, found $m/z$ = 275.1305.

### Compound 4

Under Ar atmosphere, compound **3** (350.0 mg, 1.0 mmol), $PdCl_2(PPh_3)_2$ (21.0 mg, 0.03 mmol), $PPh_3$ (13.1 mg, 0.05 mmol) and CuI (9.5 mg 0.05 mmol) were dissolved in triethylamine (15 mL). After stirring for a while, ethynyltrimethylsilane (0.4 mL, 3.93 mmol) was added *via* syringe. The solution was stirred at 80 °C for 4 h. After removal of solvent under reduced pressure, the residue was purified by column chromatography (silica gel, $CH_2Cl_2$/petroleum ether (30–60 °C) = 3 : 1, v/v) to give a yellow oil. Then, a mixture of product, $K_2CO_3$ (2.0 g 1.5 mmol), $CH_2Cl_2$ (5 mL) and $CH_3OH$ (8 mL) was stirred at rt for 6 h. The white turbid liquid was washed with water and the aqueous phase was extracted with $CH_2Cl_2$. After removal of solvent under reduced pressure, the residue was purified with column chromatography (silica gel; $CH_2Cl_2$/petroleum ether (30–60 °C) = 1 : 3, v/v) to give 195.0 mg of **3** as a white powder. The overall yield was 79%; m.p. = 46.8–48.3 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.27 (s, 1H), 8.09 (d, 1H, $J$ = 7.6 Hz), 7.61 (d, 1H, $J$ = 8.4 Hz), 7.51 (t, 1H, $J_1$ = 8.0 Hz, $J_2$ = 8.4 Hz), 7.42 (d, 1H, $J$ = 8.0 Hz), 7.35 (d, 1H, $J$ = 8.4 Hz), 7.28 (t, 1H, 8.4 Hz), 4.30 (t, 2H, 7.2 Hz), 3.09 (s, 1H), 1.88–1.81 (m, 2H), 1.42–1.37 (m, 2H), 0.97 (t, 3H, 7.2 Hz); TOF HRMS EI$^+$: $C_{18}H_{17}N^+$, calculated $m/z$ = 247.1361, found $m/z$ = 247.1351.

### Compound 6

Under Ar atmosphere, compound **2** (65.0 mg, 0.24 mmol), compound **5a** (35.0 mg, 0.08 mmol), $PdCl_2(PPh_3)_2$ (7.0 mg, 0.01 mmol), $PPh_3$ (5.3 mg, 0.02 mmol) and CuI (3.8 mg 0.02 mmol) were dissolved in triethylamine (10 mL). The solution was stirred at 60 °C for 6 h. After removal of solvent under reduced pressure, the residue was purified by column chromatography (silica gel, DCM/petroleum ether (30–60 °C) = 3 : 1, v/v) to give 30.3 mg of **6** as a dark red powder. Yield: 65%; m.p. = 236.8–237.9 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 10.09 (s, 1H), 8.58 (s, 1H), 8.25 (d, 1H, $J$ = 8.4 Hz), 7.62 (d, 1H, $J$ = 8.4 Hz), 7.53–7.51 (m, 3H), 7.49 (d, 1H, $J$ = 8.4 Hz), 7.40 (d, 1H, $J$ = 8.4 Hz), 7.32–7.30 (m, 2H), 6.04 (s, 1H), 4.35 (t, 2H, $J$ = 7.6 Hz), 2.76 (s, 3H), 2.59 (s, 3H), 1.90–1.83 (m, 2H), 1.55 (s, 3H), 1.42–1.36 (m, 5H), 0.97 (t, 3H, 7.2 Hz); TOF HRMS LD$^+$: $C_{38}H_{34}BF_2N_3O^+$, calculated $m/z$ = 597.2763, found $m/z$ = 597.2758.

### C-1

Under Ar atmosphere, compound **6** (30.0 mg, 0.05 mmol) and sarcosine (13.4 mg, 0.15 mmol) were added to the solution of $C_{60}$ (43.0 mg, 0.06 mmol) in toluene (30 mL). The mixture was heated to 110 °C, and was refluxed for 12 h, then cooled slowly to rt. The solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel, $CH_2Cl_2$/petroleum ether (30–60 °C) = 3 : 1, v/v) to give 20.0 mg of **C-1** as a dark red powder. Yield: 30%; m.p. > 250 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.25 (s, 1H), 7.55–7.50 (m, 5H), 7.33–7.29 (m, 5H), 6.02 (s, 1H), 5.10–5.03 (m, 2H), 4.32–4.25 (m, 3H), 2.84 (s, 3H), 2.75 (s, 3H), 2.58 (s, 3H), 1.88–1.80 (m, 2H), 1.53 (s, 3H), 1.42–1.37 (m, 5H), 0.98–0.92 (m, 3H); TOF HRMS LD$^+$: $C_{100}H_{39}BF_2N_4^+$, calculated $m/z$ = 1344.3236, found $m/z$ = 1344.3181.

### Compound 7

Under Ar atmosphere, compound **2** (70.0 mg, 0.25 mmol), compound **5b** (86.4 mg, 0.15 mmol), PdCl2(PPh3)2 (7.0 mg, 0.01 mmol), $PPh_3$ (5.3 mg, 0.02 mmol) and CuI (3.8 mg 0.02 mmol) were dissolved in triethylamine (10 mL). The solution was stirred at 60 °C for 6 h. After removal of solvent under reduced pressure, the residue was purified by column chromatography (silica gel, $CH_2Cl_2$/petroleum ether (30–60 °C) = 1 : 1, v/v) to give 40.0 mg of **7** as a dark purple powder. Yield: 37%; m.p. > 250 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 10.09 (s, 1H), 8.58 (s, 1H), 8.25 (d, 1H, $J$ = 8.4 Hz), 7.62 (d, 1H, $J$ = 8.4 Hz), 7.55–7.53 (m, 3H), 7.49 (d, 1H, $J$ = 8.4 Hz), 7.40 (d, 1H, $J$ = 8.4 Hz), 7.30–7.28 (m, 2H), 4.35–4.31 (t, 2H, $J_1$ = $J_2$ = 7.6 Hz), 2.77 (s, 3H), 2.67 (s, 3H), 1.90–1.83 (m, 2H), 1.55 (s, 3H), 1.41–1.36 (m, 5H), 0.97–0.94 (t, 3H, $J1$ = $J2$ = 7.4 Hz); TOF HRMS LD+: $C_{38}H_{33}BF_2N_3OI^+$, calculated $m/z$ = 723.1730, found $m/z$ = 723.1675.

### Compound 8

Under argon atmosphere, compound **7** (30.0 mg, 0.04 mmol), compound **4** (100.0 mg, 0.40 mmol), PdCl2(PPh3)2 (3.5 mg, 0.005 mmol), PPh3 (2.6 mg, 0.01 mmol) and CuI (1.9 mg 0.01 mmol) were dissolved in triethylamine (10 mL). The solution was stirred at 60 °C for 6 h. After removal of solvent under reduced pressure, the residue was purified by column chromatography (silica gel, $CH_2Cl_2$/petroleum ether (30–60 °C) = 1 : 1, v/v) to give 20.0 mg of **8** as a dark purple powder. Yield: 53%; m.p. > 250 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 10.09 (s, 1H), 8.58 (s, 1H), 8.25 (s, 1H), 8.20 (s, 1H), 8.08 (d, 1H, $J$ = 7.2 Hz), 8.03 (d, 1H, $J$ = 7.2 Hz), 7.62 (d, 1H, $J$ = 8.4 Hz), 7.56–7.54 (m, 4H), 7.48–7.46 (m, 2H), 7.41–7.38 (m, 2H), 7.35–7.33 (m, 3H), 7.24 (d, 1H, $J$ = 7.8 Hz), 4.32–4.29 (m, 4H), 2.79 (s, 6H), 1.88–1.82 (m, 4H), 1.58 (s, 6H), 1.41–1.36 (m, 4H), 0.96–0.94 (m, 6H); TOF HRMS LD$^+$: $C_{56}H_{49}BF_2N_4O^+$, calculated $m/z$ = 842.3967, found $m/z$ = 824.3987.

### C-2

Under Ar atmosphere, compound **8** (42.0 mg, 0.05 mmol) and sarcosine (14.0 mg, 0.16 mmol) were added to the solution of $C_{60}$ (43.0 mg, 0.06 mmol) in toluene (30 mL). The mixture was heated to 115 °C, and was refluxed for 12 h, then cooled slowly to ambient temperature. The solvent was then removed under reduced pressure. The residue was purified by column chromatography (silica gel, $CH_2Cl_2$/petroleum ether (30–60 °C) = 2 : 1, v/v) to give 22.0 mg of **C-2** as a dark purple powder. Yield: 28%; m.p. > 250 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.25 (s, 1H), 8.17

(s, 1H), 8.03 (s, 1H), 7.52–7.36 (m, 9H), 7.30–7.24 (m, 6H), 5.07–5.00 (m, 2H), 4.28–4.24 (m, 5H), 2.81 (s, 3H), 2.75 (s, 6H), 1.83–1.79 (m, 4H), 1.53 (s, 6H), 1.38–1.35 (m, 4H), 0.92–0.89 (m, 6H); TOF HRMS LD$^-$: $C_{118}H_{54}BF_2N_5^+$, calculated $m/z = 1589.4440$, found $m/z = 1589.4567$.

### L-1

Under Ar atmosphere, compound **4** (100.0 mg, 0.40 mmol), compound **5a** (45.0 mg, 0.1 mmol), $PdCl_2(PPh_3)_2$ (7.0 mg, 0.01 mmol), $PPh_3$ (5.3 mg, 0.02 mmol) and CuI (3.8 mg 0.02 mmol) were dissolved in triethylamine (12 mL). The solution was stirred at 60 °C for 6 h. After removal of solvent under reduced pressure, the residue was purified by column chromatography (silica gel, $CH_2Cl_2$/petroleum ether (30–60 °C) = 1 : 1, v/v) to give 40.0 mg of **L-1** as a dark red powder. Yield: 70%; m.p. 246.7–248.8 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.20 (s, 1H), 8.08 (d, 1H, $J = 7.6$ Hz), 7.56 (d, 1H, $J = 8.0$ Hz), 7.52–7.50 (m, 3H), 7.47 (d, 1H, $J = 7.2$ Hz), 7.40 (d, 1H, $J = 8.0$ Hz), 7.34–7.29 (m, 3H), 7.23 (d, 1H, $J = 7.2$ Hz), 6.02(s, 1H), 4.30 (t, 2H, $J = 7.2$ Hz), 2.76 (s, 3H), 2.59 (s, 3H), 1.88–1.80 (m, 2H), 1.55 (s, 3H), 1.42–1.35 (m, 5H), 0.95 (t, 3H, $J = 7.4$ Hz); TOF HRMS LD$^+$: $C_{37}H_{34}BF_2N_3^+$, calculated $m/z = 569.2814$, found $m/z = 569.2864$.

### Compound L-2

Under Ar atmosphere, compound **4** (200.0 mg, 0.81 mmol), compound **5b** (57.5 mg, 0.1 mmol), $PdCl_2(PPh_3)_2$ (7.0 mg, 0.01 mmol), $PPh_3$ (5.3 mg, 0.02 mmol) and CuI (3.8 mg 0.02 mmol) were dissolved in triethylamine (15 mL). The solution was stirred at 60 °C for 6 h. After removal of solvent under reduced pressure, the residue was purified by column chromatography (silica gel, $CH_2Cl_2$/petroleum ether (30–60 °C) = 1 : 1, v/v) to give 45.0 mg of **L-2** as a dark purple powder. Yield: 56%; m.p. > 250 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.21 (s, 2H), 8.09 (d, 2H, $J = 7.2$ Hz), 7.57 (m, 6H), 7.48 (d, 2H, $J = 7.0$ Hz), 7.41 (d, 2H, $J = 8.4$ Hz), 7.35 (m, 3H), 7.24 (d, 2H, $J = 7.8$ Hz), 4.31 (t, 4H, $J = 7.2$ Hz), 2.79 (s, 6H), 1.88–1.81 (m, 4H), 1.58 (s, 6H), 1.41–1.36 (m, 4H), 0.96 (t, 6H, $J = 7.2$ Hz); TOF HRMS LD$^+$: $C_{55}H_{49}BF_2N_4^+$, calculated $m/z = 814.4018$, found $m/z = 814.3972$.

### Triplet–triplet annihilation upconversion

A diode pumped solid state (DPSS) laser (532 and 589 nm, continuous wave) was used for the upconversions. The diameter of the laser spot is *ca.* 3 mm. The samples were purged with $N_2$ or Ar for at least for 15 min before measurement and the gas flow was maintained during the measurement. The upconversion quantum yields ($\Phi_{UC}$) were determined with the prompt fluorescence of 2,6-diiodo-bodipy (compound **5b**, Scheme 1) ($\Phi$ = 2.7% in MeCN) and **BisBDPI** as the standards (the structure is shown in Scheme 1, $\Phi_F$ = 10.5% in toluene). In order to repress the scattered laser, a black box was put behind the fluorescent cuvette to trap the laser beam.

The upconversion quantum yields were calculated with the modified equation (eqn (1)), where $\Phi_{UC}$, $A_{sam}$, $I_{sam}$, and $\eta_{sam}$ represent the quantum yield, absorbance, integrated photoluminescence intensity of the samples, the refractive index of the solvents, and where the subscript "std" is for the standard used in the measurement of the quantum yield, and "sam" for the samples to be measured.[11]

$$\Phi_{UC} = 2\Phi_{std}\left(\frac{1-10^{-A_{std}}}{1-10^{-A_{sam}}}\right)\left(\frac{I_{sam}}{I_{std}}\right)\left(\frac{\eta_{sam}}{\eta_{std}}\right)^2 \quad (1)$$

In the above equation the absorption correction factor $1\text{–}10^{-A}$ was used instead of the absorbance ($A$) because the absorbances of the samples are much higher than those usually used for determination of luminescence quantum yields. The absorbances of the samples used for the determination of the upconversion quantum yields are 0.2611, 0.3294, 0.3008, and 0.0343 for **C-1**, **5b**, **C-2** and **BisBDPI**, respectively.

The CIE coordinates ($x$, $y$) of the emission of the sensitizers alone and the emission of the upconversion were derived from the emission spectra with the software of CIE Color Matching Linear Algebra.

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. Wavelength is tuneable from 210 to 355 nm and from 420 to 2200 nm. OPOTEK, USA), which was synchronized to a FLS920 spectrofluorometer (Edinburgh, UK). The pulsed laser was sufficient to sensitize the TTA upconversion. The decay kinetics of the upconverted fluorescence (delayed fluorescence) were monitored with a FLS920 spectrofluorometer (synchronized to the OPO laser). The prompt fluorescence lifetime of the triplet acceptor perylene was measured with an EPL picosecond pulsed laser (405 nm) which was synchronized to the FLS 920 spectrofluorometer.

### DFT calculations

The geometries of the compounds were optimized using density functional theory (DFT) with 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. Toluene was used as solvent in the calculations (PCM model). All these calculations were performed with Gaussian 09W.[77]

## Acknowledgements

We thank the NSFC (20972024 and 21073028), the Royal Society (UK), the NSFC (China-UK Cost-Share Science Networks, 21011130154), the Fundamental Research Funds for the Central Universities (DUT10ZD212), the Ministry of Education (NCET-08-0077, and Dalian University of Technology for financial support.

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