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Selective population of triplet excited states in heavy atom free BODIPY- C₆₀ based molecular assemblies

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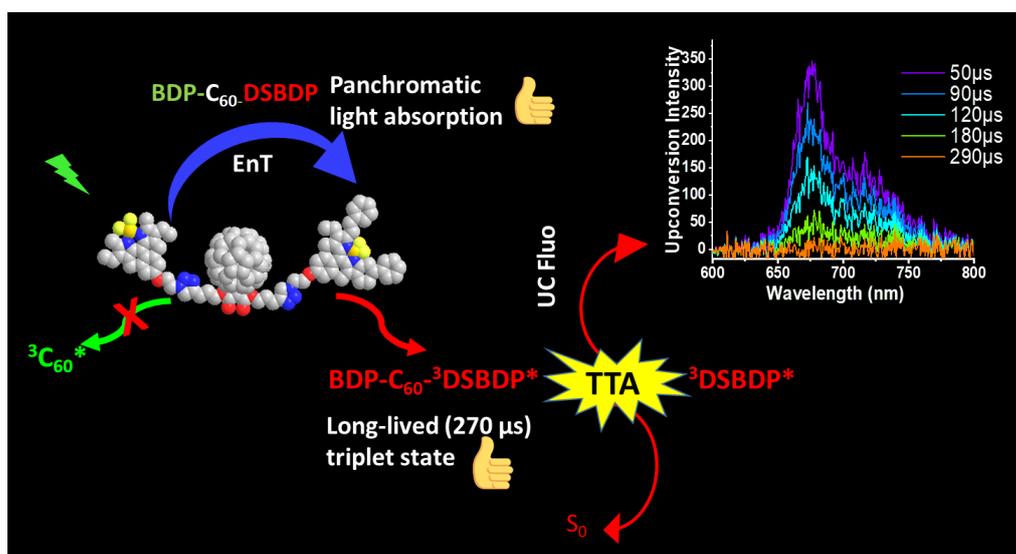
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Graphical abstract

Abstract: Photophysical studies on a BODIPY-fullerene-distyryl BODIPY triad (BDP-C₆₀-DSBDP) and its reference dyads (BODIPY-fullerene; BDP-C₆₀ and distyryl BODIPY-fullerene; DSBDP-C₆₀) are presented herein. In the triad, the association of the two chromophore units linked by a fullerene moiety leads to strong near UV-visible light absorption from 300 nm to 700 nm. The triplet excited state was observed upon visible excitation in all these assemblies, and shown to be localized on the C₆₀ or BODIPY moieties depending on the structure of the BODIPY chromophore. Using quantitative nanosecond transient absorption, we provide a complete investigation on the lifetime and formation quantum yield of the triplet excited state. In the BDP-C₆₀ dyad, the triplet excited state of C₆₀ ($\tau = 7 \pm 1 \mu\text{s}$) was obtained with a quantum yield of $40 \pm 8 \%$. For the DSBDP-C₆₀ dyad and BDP-C₆₀-DSBDP triad, a longer-lived triplet excited state with a lifetime of around $250 \pm 20 \mu\text{s}$ centered on the DSBDP moiety was formed, with respective quantum yields of 37 ± 8 and $20 \pm 4 \%$. Triplet-triplet annihilation up-conversion is characterized in the BDP-C₆₀ dyad and the bichromophoric triad in the presence of perylene and DSBDP-monomer as respective annihilators. The photo-induced formation of a long-lived ³DSBDP* in the triad coupled with panchromatic light absorption offers potential applications as a heavy-atom-free organic triplet photosensitizer.

Keywords: BODIPY, fullerene, triplet state, excited state, triplet formation quantum yield, fluorescence lifetime, triplet lifetime, transient absorption.

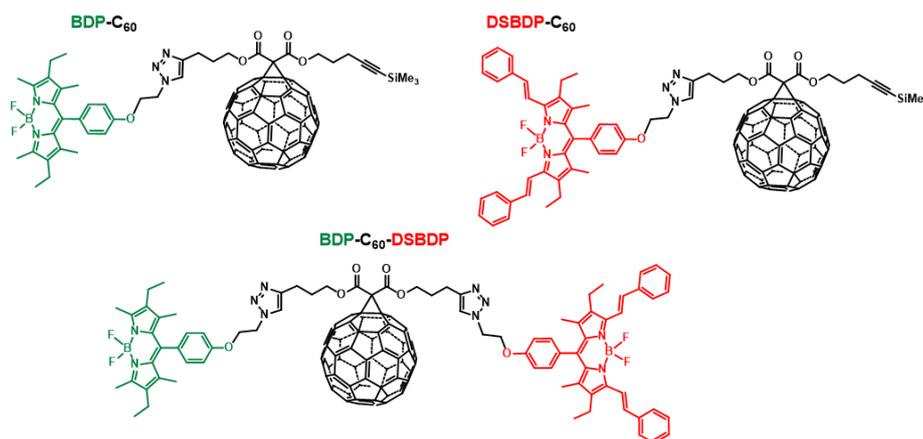
1. Introduction

Triplet photosensitizers have gained much attention due to their wide range of applications in photocatalysis^{1,2}, photodynamic therapy^{3,4} and triplet-triplet annihilation (TTA) upconversion^{5,6}. A quintessential triplet photosensitizer should show broadband visible light absorption with a high absorption coefficient ($>$ several tens of thousands $\text{M}^{-1} \cdot \text{cm}^{-1}$), high triplet formation quantum yield, hypotoxicity and long-lived triplet excited states^{7,8}. Conversely, classical organic triplet photosensitizers containing transition metal atoms, able to populate triplet excited states suffer from the drawbacks of short lifetimes (typically several microseconds) and weak absorption in the visible range^{9,10}, in addition to being expensive. Other frequently explored triplet photosensitizers consist of heavy halogen atom (Br, I) substituted organic chromophores, resulting in shortened triplet excited state lifetimes on account of increased spin-orbit coupling^{11,12,13}. Meanwhile, the development of heavy-atom free organic triplet photosensitizers remains a challenge, mainly due to the difficulty in

predicting their inter-system crossing (ISC) ability upon derivitization^{7,14,15}. Moreover, the conventional triplet photosensitizers are mono-chromophoric, limiting their absorption in the entire visible spectral range. In order to deal with the above mentioned deleterious effects, one of the important strategies for devising heavy-atom-free triplet organic photosensitizers makes use of multi-chromophores in conjunction with an electron spin convertor to serve a dual purpose: wide spectral absorption with an efficient ISC^{7,8}. Along these lines, fullerene (C₆₀) derivatives are frequently employed as efficient spin convertors due to their high ISC efficiency, rounding-up to unity¹⁶. Even so, fullerene itself cannot be used as a model photosensitizer owing to its weak visible light absorption, but the existence of a low-lying singlet excited state can be exploited to realize singlet energy transfer from organic chromophores to C₆₀^{15,17}. The choice of organic chromophores has been greatly directed towards boron-dipyrromethene (BODIPY) in light of its photophysical properties (strong visible-light absorption, photostability, high fluorescence quantum yields) and easy functionalization that in turn facilitates absorption tunability over the whole visible range^{18,19,20}. Consequently, BODIPY-C₆₀ based molecular motifs are of particular interest for the formation of a triplet excited state upon photoexcitation of a chromophore entity.

A number of BODIPY-C₆₀ based molecular combinations have been reported, featuring the mechanistic traits of triplet state formation depending upon the polarity of the solvent and triplet energy levels^{21,22,23,24,25}. In non-polar solvents, singlet energy transfer from BODIPY to fullerene populates the singlet excited state of C₆₀, which then undergoes an ISC to populate the triplet excited state of C₆₀^{15,21,22,26}. Further, a back triplet energy transfer can occur from C₆₀ to triplet BODIPY in what is known as “ping-pong” energy transfer^{15,23}. In polar solvents, charge recombination may be responsible for triplet population of either the BODIPY or C₆₀^{21,24}. A formerly reported broadband light-absorbing triad and tetrad (450-650 nm) demonstrated excitation energy funneling to C₆₀, followed by an ISC to populate the C₆₀ triplet excited state, finally resulting in the population of the triplet excited state of BODIPY with a lifetime of about 132.9 μs²³. However, the authors did not characterize the efficiency of the triplet excited state formation. Another recently published supramolecular triad containing two BODIPY units and a fullerene enabled the absorption of panchromatic light but its ability to induce a triplet excited state was not explored²⁷. Despite these previous reports, to our knowledge, panchromatically absorbing heavy-atom-free BODIPY-C₆₀-based molecular systems have barely been investigated for their triplet excited state properties.

The present work reports photophysical investigations of a novel BODIPY-fullerene-distyryl BODIPY panchromatic light-absorbing triad (BDP-C₆₀-DSBDP) and its associated dyads (BODIPY-fullerene; BDP-C₆₀ and distyryl BODIPY-fullerene; DSBDP-C₆₀) (Scheme 1). The synthesis of the triad, following a new synthetic approach of grafting two differently functionalized BODIPY cores on two clickable arms of a fullerene platform using alkyne-azide click chemistry, was reported previously²⁸. The presence of two chromophore units enables broad absorption of the system in the visible region. The population of a triplet excited state upon visible excitation in the two isolated dyads and the triad was confirmed by employing nanosecond time-resolved spectroscopy. For the BDP-C₆₀ dyad, excitation at 525 nm of the BDP unit populated the triplet excited state localized on the C₆₀ moiety. However, in the DSBDP-C₆₀ dyad, excitation of the DSBDP unit allowed the population of a long-lived triplet excited state localized on the DSBDP moiety. Moreover, the BDP-C₆₀-DSBDP triad results in the population of long-lived triplet state on the DSBDP, regardless of selective excitation of the two chromophore units, while leveraging the panchromatic light absorption at the same time. To demonstrate the potential application of this long-lived triplet state photosensitizer in these systems, triplet-triplet annihilation up-conversion, occurring upon energy transfer from the triplet states to a triplet acceptor/annihilator, is shown.



Scheme 1. Structure of the BDP-C₆₀-DSBDP triad, BDP-C₆₀ and DSBDP-C₆₀ dyads under study.

2. Materials and methods

Materials

All the molecular systems (BDP, DSBDP, methanofullerene platform, BDP-C₆₀, DSBDP-C₆₀ and BDP-C₆₀-DSBDP triad) were synthesized at Institut Lavoisier de Versailles following the procedures described by Allard *et al.*²⁸

Spectroscopic grade benzonitrile, toluene and ethyl iodide were purchased from Sigma-Aldrich and used without further purification.

Steady-state and time-resolved fluorescence measurements

Steady-state absorption measurements were carried out using UV-2600, a UV-Vis spectrophotometer from SHIMADZU. 10 x 10 mm² quartz cells were used for steady state measurements. Emission and excitation spectra were recorded using Scientific Fluoromax PLUS (Horiba Jobin-Yvon) under right angle configuration with a bandwidth of 1 nm in excitation and 2 nm in emission.

In order to minimize the error in the estimation of fluorescence quantum yields, three different concentrations were measured (absorbance < 0.1 to avoid reabsorption and inner filter effects)²⁸. Briefly, the integral area of the emission of a sample molecule and its corresponding reference at each concentration was plotted as a function of the respective absorbance at the excitation wavelength. The slopes obtained by the linear regression analysis were used to calculate the fluorescence quantum yield of the molecule using Equation (1):

$$\phi_M = \frac{\text{slope}_S}{\text{slope}_R} \times \left(\frac{\eta_S}{\eta_R}\right)^2 \times \phi_R \quad (1)$$

where η is the refractive index of the solvent and subscripts S and R denote the sample molecule and reference respectively, ϕ_R is the fluorescence quantum yield of the reference. Using this method, an error of 10 % was estimated in the calculation of fluorescence quantum yields.

Fluorescence decay curves were obtained using the same set-up previously described by Ghose *et al.*³⁰ with two different excitations: (i) 495 nm femtosecond excitation pulses (<200 fs, FWHM, 4 Mhz) obtained with a Ti:sapphire laser (Coherent Chameleon Ultra II, 80 MHz) coupled to a pulse picker (4 MHz) and a harmonic generator (SHG/THG, APE) and (ii) 635 nm picosecond excitation pulse (Picoquant laser diode) emitting with a pulse width <90ps (FWHM) and a repetition rate of 8 MHz. Photon counting was performed using a PicoHarp 300 TC-SPC system (PicoQuant) with a bin time of 4 ps. The IRF (instrumental response function) of the setup was measured using a LUDOX colloidal solution and measurements were performed using a FluoTime 200 spectrometer (4 nm bandpass) and polarizers were set at magic angle. Solutions with an absorbance below 0.1 (1 cm path length) at excitation wavelengths

were used. The emission decays were collected until 10000 counts at the maximum. They were analyzed with a weighted sum of exponential decay convolved by the IRF using the FluoFit software (PicoQuant). The quality of the fits was assessed by the value of χ^2 (<1.1) and the residuals autocorrelation function. The amplitude weighted mean lifetime of the molecules were obtained using: $\tau_m = \sum A_i \tau_i / \sum A_i$.

Transient absorption spectroscopy

All the measurements were performed under argon saturation using a quartz cuvette of dimensions 10 mm x 4 mm. For laser flash photolysis, an optical parametric oscillator (OPO) pumped by a pulsed nanosecond Nd:YAG laser (Quanta-Ray INDI series) was used to excite the samples. The pump laser was operated at 10Hz. The resulting pulse width was 4 ns and the energy was about 1-2 mJ/pulse. A white light super continuum laser (STM-2-UV LEUKOS) was used as a probe light for transient absorption measurements. The probe laser was operated at a repetition rate of 20 Hz. The probe beam was split by means of a beam splitter that directs one part of beam to the sample cell while the other is directed towards the reference, to monitor spectral energy distribution fluctuations. The transmitted light from the sample enters into the center of the optical fiber (round-to-linear) bundle that goes to a spectrograph (SPEX 270M, Jobin-Yvon) for analysis. The dispersed white light from the spectrograph is detected by an intensified charge coupled device (ICCD) camera PIMAX-4 (Princeton Instrument). The spectrograph simultaneously records the reference and sample spectra. The ICCD area vertically receives a bundle of 18 optical fibers of which 9 are from the sample and 9 from the reference. ICCD records the spectra with the same frequency as the probe (20 Hz). Upon varying the delay time between pump and probe, the transient absorption spectra with and without pump can be recorded using Equation (2):

$$\Delta A = \log_{10} \left(\frac{s_{ref}^p}{s_{ref}^0} \times \frac{s_{sample}^0}{s_{sample}^p} \right) \quad (2)$$

where s_{ref}^p and s_{ref}^0 are reference spectra with and without pump respectively while, s_{sample}^p and s_{sample}^0 are sample spectra with and without pump respectively.

Calculation of triplet quantum yields

The triplet states have been quantified using the relative actinometry method³¹, using an aqueous solution of tris(2,2'-bipyridine)ruthenium(II) [Ru(bpy)₃]²⁺ as a reference. Transient absorption changes upon decreasing the excitation power were recorded for the reference and corresponding dyad and triad molecules, under exactly the same experimental conditions (λ_{exc} ,

optical path, absorbance etc.). Transient absorption decays at 455 nm for $[\text{Ru}(\text{bpy})_3]^{2+}$ (maximum of ground state bleach) and the triplet state absorption maxima (710 nm for BDP- C_{60} dyad and 710 nm for DSBDP- C_{60} dyad and BDP- C_{60} -DSBDP triad) were recorded. **Fig. SI-1** shows ΔA versus power (mW) plots for ${}^3\text{C}_{60}^*$ (**Fig. SI-1a**) and ${}^3\text{DSBDP}^*$ (**Fig. SI-1b**) in the dyad and the triad, along with that of $[\text{Ru}(\text{bpy})_3]^{2+}$. For each excitation power, ΔA values have been noted at the maxima of the kinetic curves at 710 nm for ${}^3\text{C}_{60}^*$ and 455 nm for $[\text{Ru}(\text{bpy})_3]^{2+}$ (**Fig. SI-2**), 710 nm for ${}^3\text{DSBDP}^*$ and 455 nm for $[\text{Ru}(\text{bpy})_3]^{2+}$ (**Fig. SI-3**). Putting in the values of slopes obtained by linear regression in the Equation (3) given below, triplet quantum yields were obtained

$$\Phi_T = \frac{\text{slope}_T \times \Phi_{\text{ref}} \times \Delta\varepsilon_{\text{ref}}}{\text{slope}_{\text{ref}} \times \Delta\varepsilon_T} \quad (3)$$

where T is the triplet whose quantum yield is to be calculated and Φ_{ref} is the formation quantum yield of $[\text{Ru}(\text{bpy})_3]^{2+}$ ($\Phi_{\text{ref}} \sim 1$), $\Delta\varepsilon_{\text{ref}}$ is the absolute value of molar absorption coefficient for the $[\text{Ru}(\text{bpy})_3]^{2+}$ reference ground state bleach ($\Delta\varepsilon_{455} = -10100 \text{ M}^{-1} \cdot \text{cm}^{-1}$)^{32,33}, $\Delta\varepsilon_T$ is the value of molar absorption coefficient for ${}^3\text{C}_{60}^*$ ($16\,100 \text{ M}^{-1} \cdot \text{cm}^{-1}$)³⁴ or ${}^3\text{DSBDP}^*$ ($58\,000 \text{ M}^{-1} \cdot \text{cm}^{-1}$).

3. Results and discussion

Steady-state absorption and fluorescence studies

The absorption spectra of the BDP- C_{60} -DSBDP triad and its related dyads in benzonitrile are shown in **Fig. 1a**. Their photophysical parameters are summarized in **Table 1**. The absorption spectra of the parent compounds BDP- N_3 and DSBDP- N_3 and the methanofullerene platform (C_{60}) in benzonitrile are presented in the supplementary information (**Fig. SI-4**). The fullerene building block shows typical absorption spectrum of methanofullerene with an intense band at 330 nm and a small sharp band at 428 nm³⁵. The main absorption band of the BDP located at 527 nm corresponds to the $\text{S}_0\text{-S}_1$ transition in phenyl-substituted BDPS^{36,37} whereas a weaker and broader feature at 380 nm corresponds to the $\text{S}_0\text{-S}_2$ transition³⁷ (**Fig. SI-4**). The intense and large absorption band of DSBDP peaking at 637 nm is attributed to the $\text{S}_0\text{-S}_1$ transition. This band is significantly red shifted and broadened as compared to the BDP band due to the extended conjugation of the BODIPY core¹⁹. The UV bands with a maximum at 345 nm for DSBDP can be associated with the $\pi\text{-}\pi$ distyryl subunits along with a shoulder attributed to the $\text{S}_0\text{-S}_2$ transition of the BODIPY backbone.

The spectra of the BDP- C_{60} and DSBDP- C_{60} are very similar to those observed in the BDP and DSBDP moieties with in addition the expected contribution of the methanofullerene, *i.e.* a strong band in the UV region at 330 nm and a small sharp band at 428 nm (**Fig. 1a**). The

absorption of the BDP-C₆₀ and DSBDP-C₆₀ dyads is therefore the sum of the absorbance of fullerene and the respective BDPs (**Fig. SI-5a**). Similarly, the absorption spectrum of the triad almost overlaps with the sum of the corresponding reference compound spectra, signifying negligible ground-state interaction between BDPs and the fullerene moiety (**Fig. SI-5b**). This relates to the limited electronic coupling between the BDPs and the fullerene due to the absence of conjugation, as already observed in a similar BDP-C₆₀ dyad³⁸.

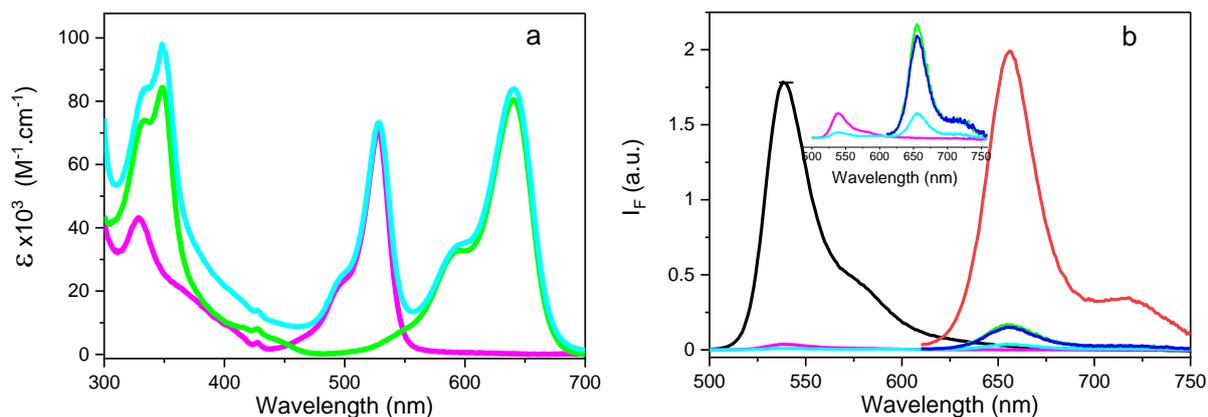


Fig. 1. a. Absorption spectra of BDP-C₆₀ (pink), DSBDP-C₆₀ (green) and DSBDP-C₆₀-BDP (cyan) in benzonitrile. **b.** Emission spectra in benzonitrile of BDP (black, $\lambda_{\text{exc}}=495$ nm), DSBDP (red, $\lambda_{\text{exc}}=605$ nm). **Inset:** BDP-C₆₀ (pink, $\lambda_{\text{exc}}=495$ nm), DSBDP-C₆₀ (green, $\lambda_{\text{exc}}=605$ nm), and DSBDP-C₆₀-BDP (cyan, $\lambda_{\text{exc}}=495$ nm; blue, $\lambda_{\text{exc}}=605$ nm).

Upon exciting the parent BDP in benzonitrile, a strong fluorescence band centered at 537 nm was obtained with a high quantum yield of 73 % (**Fig. 1b**). However, the BDP emission intensity was critically reduced by over 98 % in the BDP-C₆₀ dyad giving a quantum yield of 1.5 %. This observation is characteristic of excited state energy transfer and/or electron transfer events from the BDP antenna to C₆₀. Indeed the energy transfer from BDP to C₆₀ must be taken into consideration due to the spectral overlap between BDP emission and C₆₀ absorption. Likewise, DSBDP-N₃ excited at 605 nm gave an intense fluorescence band at 650 nm with a fluorescence quantum yield (Φ_{F}) of 85 %, which was also greatly quenched by 92 % in the dyad where DSBDP was attached to C₆₀ ($\Phi_{\text{F}} = 7.2$ %). In addition, upon exciting the DSBDP-C₆₀-BDP triad at 495 nm, corresponding mainly to the absorption of the BDP chromophore, the emission of the BDP subunit at 537 nm was quenched by over 99% ($\Phi_{\text{F}} = 0.4$ %), with the appearance of a more intense emission band at around 650 nm. This band was assigned to DSBDP emission by comparison with the reference fluorescence spectrum of DSBDP (red curve **Fig.1-b**), suggesting the occurrence of energy transfer from ¹BDP* to DSBDP. In addition, the excitation spectra of the two dyads almost completely corresponds to their

respective BODIPY absorption spectra and the excitation spectra of pristine BODIPYs, indicating that the BODIPY moieties are responsible for the emission of the dyads (**Fig. 2a, b** and **Fig. SI-6**). However, the excitation spectrum of the triad observed at the emission of DSBDP moiety ($\lambda_{em} = 670$ nm) clearly shows the contribution of the BDP moiety ($\lambda_{abs} = 525$ nm) in addition with that of DSBDP ($\lambda_{abs} = 637$ nm), confirming the energy transfer process from the BDP to DSBDP (**Fig. 2c**). Also, the excitation spectrum of the BDP- C_{60} dyad at 670 nm monitoring wavelength reveals the negligible contribution of BDP emission, confirming that the energy transfer process from BDP to DSBDP is solely responsible for the DSBDP emission band in the triad (**Fig. SI-7**). Scheme 2 resumes the different possible photoinduced processes occurring upon excitation of the BDP/DSBDP chromophores.

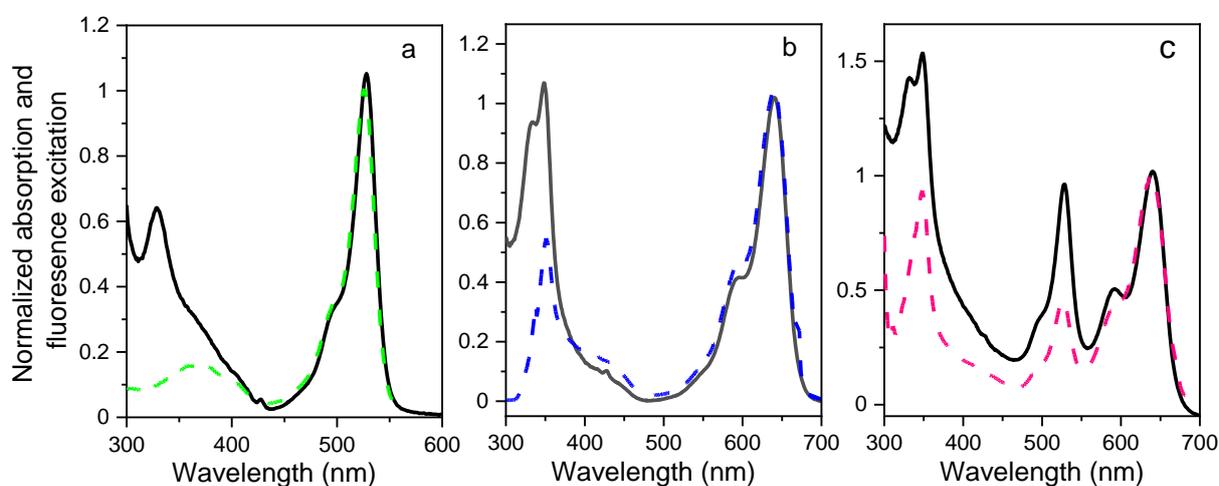
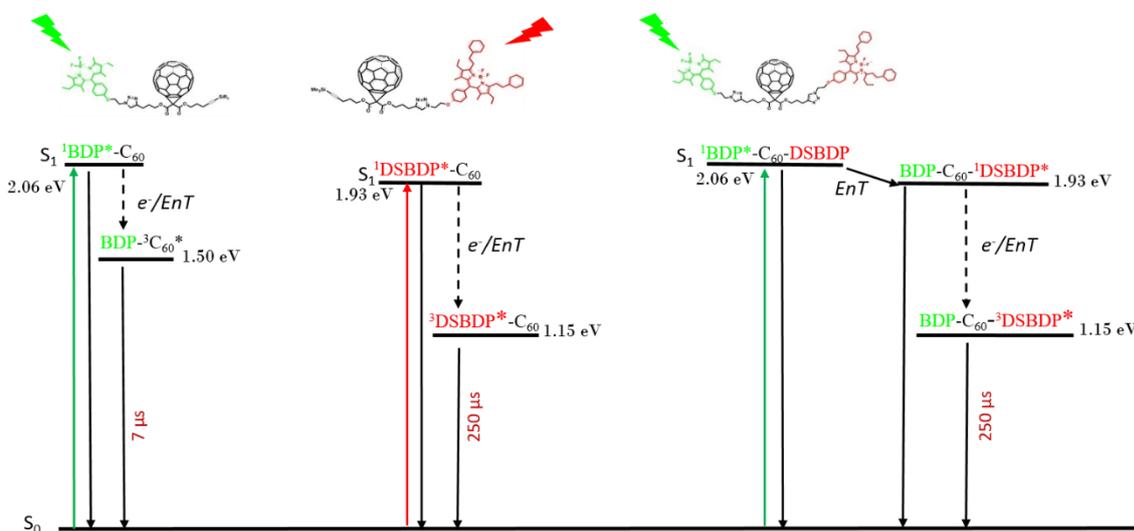


Fig. 2. Excitation spectra of **a.** BDP- C_{60} dyad ($\lambda_{em} = 560$ nm; dashed green), **b.** DSBDP- C_{60} dyad ($\lambda_{em} = 670$ nm; dashed blue), and **c.** BDP- C_{60} -DSBDP triad ($\lambda_{em} = 670$ nm; dashed pink), overlapped with their respective absorption spectra; black solid curves.



Scheme 2. Simplified relaxation pathways upon excitation of BDP and DSBDP in the BDP-C₆₀ and DSBDP-C₆₀ dyads and in the BDP-C₆₀-DSBDP triad. e⁻T: electron transfer, EnT: energy transfer. Dashed arrows present potential processes that were not observed in this study.

In order to further understand the quenching of the BODIPY moieties in the dyads and the triad, time-correlated single photon counting (TCSPC) measurements were performed in benzonitrile. The fluorescence decays of the parent BODIPY and of the two dyads and triad are shown in **Fig. 3** and **Fig. SI-8**. The fluorescence decay of the parent compounds can be fitted by a monoexponential function with lifetimes of 4.57 and 4.46 ns for BDP and DSBDP respectively, characteristic of the BODIPY singlet excited state lifetime³⁸ (**Table 1**). However, the decays of the dyads and triad are no longer monoexponential, with the contribution of several short components. The mean lifetimes were significantly reduced in the two dyads and the triad (**Table 1**), indicating some rapid electron and/or energy transfer events taking place in the excited state of the BODIPY moieties. A similar lifetime was obtained for DSBDP emission either for the DSBDP-C₆₀ dyad or the triad regardless of the excitation wavelength, suggesting a similar deactivation pathway from ¹DSBDP* in the two systems. However, we observed a decrease in lifetime of BDP emission in the triad as compared to that of the BDP-C₆₀ dyad, due to the additional deactivation pathway of energy transfer from BDP to DSBDP in the triad.

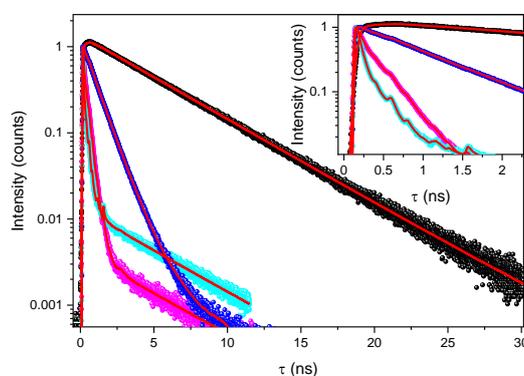


Fig. 3. Fluorescence decay of parent BDP (black, $\lambda_{exc} = 495$ nm, $\lambda_{em} = 535$ nm), BDP-C₆₀ dyad (pink, $\lambda_{exc} = 495$ nm, $\lambda_{em} = 535$ nm), BDP-C₆₀-DSBDP triad (cyan, $\lambda_{exc} = 495$ nm, $\lambda_{em} = 535$ nm; blue, $\lambda_{exc} = 495$ nm, $\lambda_{em} = 650$ nm) in benzonitrile.

Compound	λ_{abs} , nm (ϵ , M ⁻¹ cm ⁻¹)	λ_{em} , nm	Φ_F , %	τ_m , ns
C ₆₀ ^a	330(33 000), 428	697	0.05	--
BDP ^b	525(68 700)	535	73	4.57

BDP-C₆₀^b	380(14 000), 525(69 600)	535	1.5	0.15
DSBDP^c	637(70 400)	650	85	4.46
DSBDP-C₆₀^c	330, 348(77 600), 637(74 400)	650	7.2	0.66
DSBDP-C₆₀-BDP	330, 348(96 200), 525(73 200), 637(83 600)	535	0.4 ^b	0.08 ^b
		650	6.7 ^c	0.69 ^c
		650	3.0 ^d	0.67 ^d

Φ_F : Fluorescence quantum yield with 10 % error, τ_m : mean fluorescence lifetime with 10 % error

^a ref.³⁹, ^b $\lambda_{exc} = 495$ nm, $\lambda_{em} = 535$ nm, quantum yield measurement of BODIPY moiety with Rhodamine 6G used as standard ($\lambda_{exc} = 495$ nm, $\phi = 95\%$ in ethanol); ^c $\lambda_{exc} = 635$ nm, $\lambda_{em} = 650$ nm, quantum yield measurement of DSBDP moiety with Oxazine 1 used as standard ($\lambda_{exc} = 605$ nm, $\phi = 11\%$ in ethanol); ^d $\lambda_{exc} = 495$ nm, $\lambda_{em} = 650$ nm, quantum yield measurement of DSBDP moiety with [Ru(bpy)₃]²⁺ used as standard ($\lambda_{exc} = 495$ nm, $\phi = 4.2\%$ in water).

Table 1. Absorption and emission data for BDP and DSBDP systems in benzonitrile

Nanosecond time-resolved spectroscopy

To decipher the production of the triplet excited states in the dyads and triad, time-resolved nanosecond transient absorption was performed upon laser pulsed excitation. First, the transient absorption (TA) measurements were studied in reference compounds (BDP-N₃, DSBDP-N₃ and C₆₀ platform) in benzonitrile. Transient absorption bands of the excited species for BDP-N₃ and DSBDP-N₃ decay on a nanosecond timescale with a lifetime of a few nanoseconds as obtained by TCSPC measurements (**Table 1, Fig. SI-9**), indicating the presence of only singlet excited states of the BDP and DSBDP. No signatures of long-lived ³DSBDP* and ³BDP* states with microsecond lifetimes were observed. Further, excitation of the fullerene platform at 420 nm (**Fig. SI-10**) reveals two positive transient absorption bands at 400 and 710 nm characteristic of the C₆₀ triplet state¹⁶ with a lifetime of (9 ± 1) μs.

Next, a pulsed laser beam at 525 nm was used to excite the BDP moiety of the BDP-C₆₀ dyad. The TA spectra show positive transient bands at about 400 and 710 nm which are attributed to absorption of the ³C₆₀* state and decay with a lifetime of (7 ± 1) μs (**Fig. 4a**). This observation was confirmed by measurements in aerated solution: the bands of ³C₆₀* decay in a very short lifetime of about 400 ns, indicating the effect of oxygen in quenching the triplet excited state (**Fig. SI-11a**). As already reported in a similar BDP-C₆₀ dyad³⁸, the formation of a ³C₆₀* triplet state may be explained by an energy transfer from ¹BDP* to ¹C₆₀* followed by an intersystem crossing to form ³C₆₀*. **Scheme 2** summarizes the energy level and the lifetime of the triplet state in BDP-C₆₀. The triplet formation quantum yield of ³C₆₀* was then determined by applying

laser pulse relative actinometry. For this, $[\text{Ru}(\text{bpy})_3]^{2+}$ has been used as a reference due to its well defined triplet formation quantum yield close to unity³³. A triplet formation quantum yield of $40 \pm 8 \%$ was obtained for ${}^3\text{C}_{60}^*$ in the BDP- C_{60} dyad (**Fig. SI-1a and 2**). An analogous yield of ${}^3\text{C}_{60}^*$ formation (24 %) has been reported for a C_{60} -TTF dyad⁴⁰. The values of triplet state formation quantum yield for the two dyads and the triad are summarized in **Table 2**. The details of the quantum yield calculation are given in the Materials and Methods section.

Similarly, DSBDP- C_{60} was subjected to 635 nm excitation to exclusively excite the DSBDP unit. Upon excitation, the TA spectra (**Fig. 4b**) showed a bleaching band at 637 nm corresponding to the depletion of the DSBDP- N_3 ground state. In addition, the positive absorption bands at around 380, 500 and 700 nm can be attributed to ${}^3\text{DSBDP}^*$ ¹⁴. The ${}^3\text{DSBDP}^*$ formation was confirmed by measurements in an aerated solution which revealed a strong decrease in the excited state lifetime to 400 ns due to oxygen quenching (**Fig. SI-11b**). By performing transient absorption measurements on parent DSBDP- N_3 in ethyl iodide, the ${}^3\text{DSBDP}^*$ signature could also be witnessed (**Fig. SI-12**), by virtue of the heavy-atom-effect. The presence of the ${}^3\text{C}_{60}^*$ in DSBDP- C_{60} could not be excluded since its absorption is in the same spectral range, but the contribution of this species should be very low as compared to that of ${}^3\text{DSBDP}^*$. Indeed, the transient decays of DSBDP- C_{60} can be satisfactorily fitted with a monoexponential function with a lifetime of 250 μs without any contribution of the 7 μs lifetime of ${}^3\text{C}_{60}^*$. Assuming that ground state depletion leads to a 100% population of the triplet state and the absorption of the triplet state is negligible in the bleaching region (the ground state absorption band overlaps with that of bleaching at 637 nm (**Fig. SI-13**)), the differential molar absorption coefficient of ${}^3\text{DSBDP}^*$ was estimated at a maximum of 58 000 $\text{M}^{-1}\cdot\text{cm}^{-1}$. A minimum value of $37 \pm 8 \%$ was then obtained for the quantum yield of the triplet excited state formation of ${}^3\text{DSBDP}^*$ (**Fig. SI-1b and SI-3b**). The triplet excited state formation of the DSBDP can be explained by an initial thermodynamically feasible electron transfer from ${}^1\text{DSBDP}^*$ to C_{60} ($\Delta G_{\text{CS}} = -0.44$ eV estimated from the redox potentials of DSBDP and C_{60})²⁸ followed by charge recombination which populates the ${}^3\text{DSBDP}^*$, which was already observed in a DSBDP- C_{60} dyad by Fukuzumi, Ng *et al.*¹⁴ Another way to populate the DSBDP triplet state could be an initial energy transfer from ${}^1\text{DSBDP}^*$ to ${}^1\text{C}_{60}^*$ followed by ISC from ${}^1\text{C}_{60}^*$ to ${}^3\text{C}_{60}^*$ and a second energy transfer from ${}^3\text{C}_{60}^*$ to ${}^3\text{DSBDP}^*$. This ping-pong intramolecular energy transfer between DSBDP and C_{60} moieties was reported by Huang *et al.* for a DSBDP- C_{60} dyad¹⁵. Femtosecond transient absorption will be performed in a next step to decipher the formation of triplet states in these assemblies.

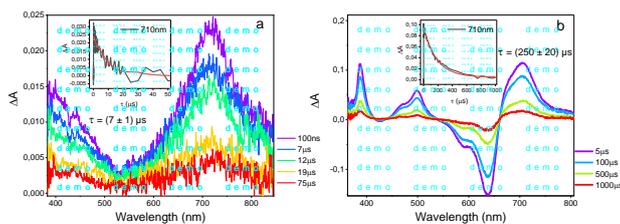


Fig. 4. a. Nanosecond transient absorption spectra of a. BDP-C₆₀ dyad (6 μM, $\lambda_{exc} = 525$ nm) and **b.** DSBDP-C₆₀ dyad in deaerated benzonitrile (6 μM, $\lambda_{exc} = 635$ nm). The inset in both the graphs shows the decay profiles at 710 nm.

In the case of the triad, selective excitation of the DSBDP unit ($\lambda_{exc} = 635$ nm) leads to triplet excited state formation on the DSBDP unit, as observed in the DSBDP-C₆₀ dyad (**Fig. SI-14**) with a similar lifetime in argon-saturated solution. The ³DSBDP* formation was confirmed by measurements in an aerated solution which revealed a strong decrease in the excited state lifetime to 400 ns due to oxygen quenching (**Fig. SI-11c**). Additionally, upon photoexcitation of the BDP unit at 525 nm, the localization of the triplet state was again detected on DSBDP (**Fig. 5 and Fig. SI-11d**). This observation confirms the excitation energy transfer from ¹BDP* to DSBDP. The triplet bands in all cases follow similar kinetics with a time constant of around (280 ± 20) μs. Using the method previously described (**Fig. SI-1b and SI-3c**), a quantum yield of (20 ± 4) % for ³DSBDP* formation was obtained in the triad. The decrease in the quantum yield value in the triad as compared to that in the dyad can be explained by the non-selective excitation of the DSBDP chromophore at 420 nm, which leads to more de-excitation pathways in the triad.

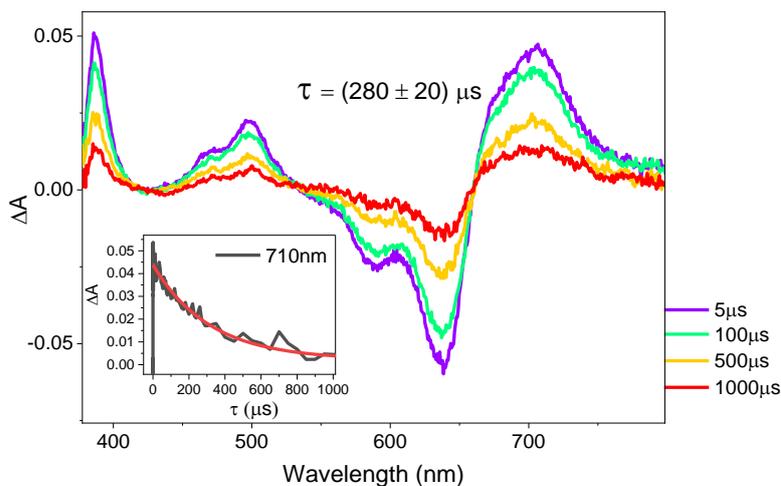


Fig. 5. Nanosecond transient absorption spectra of BDP-C₆₀-DSBDP triad (6 μM, λ_{exc} = 525 nm), in deaerated benzonitrile. Inset: Decay profile observed at 710 nm.

Remarkably, in all the events where DSBDP plays the role of the photoactive unit, the triplet state is exclusively localized on the DSBDP unit and not on C₆₀. It should be noted that direct excitation of the DSBDP reference compound does not lead to the formation of the DSBDP triplet state. As in the case of the DSBDP-C₆₀ dyad, the formation of the triplet state localized on the DSBDP in the triad upon excitation of the DSBDP may be explained either by an initial charge transfer from ¹DSBDP* to C₆₀ followed by charge recombination to populate the ³DSBDP*¹⁴ or by a ping-pong energy transfer between the DSBDP and C₆₀ moieties^{15,23}. When the BDP moiety was excited in DSBDP-C₆₀-BDP, a similar spectral signature was observed for the DSBDP-C₆₀ and the triad, suggesting the occurrence of the same processes involving the DSBDP preceded by an energy transfer from ¹BDP* to DSBDP. Unlike BDP-C₆₀ dyad, no visible signature of ³C₆₀* was observed. As in the DSBDP-C₆₀ dyad, we cannot exclude the formation of ³C₆₀* in the triad but due to the lower energy of ³DSBDP*¹⁵, it is probably the interaction between the ³C₆₀* and DSBDP on a sub-nanosecond timescale which provides a channel to the formation of ³DSBDP* in the triad.

Molecule	Triplet state	Δε, M ⁻¹ .cm ⁻¹	τ _T , μs	Φ _T , %
BDP-C₆₀	³ C ₆₀ *	16 100	7±0.8	40±8
DSBDP-C₆₀	³ DSBDP*	58 000	250±20	37±8
DSBDP-C₆₀-BDP	³ DSBDP*	58 000	280±20	20±4

Table 2. Triplet formation quantum yields estimated using laser pulse actinometry for the two dyads and the triad under study.

Application as organic triplet photosensitizer for TTA up-conversion

Triplet-triplet annihilation up-conversion (TTA-UC) was first carried out with the BDP-C₆₀ dyad that exhibits a high triplet state quantum yield in addition to a strong visible light absorption. Perylene was used as a triplet annihilator due to the comparable energy levels of ³C₆₀* (1.56eV)²¹ and the triplet of perylene (1.53eV)⁴¹ and therefore a possible triplet-triplet energy transfer (TTET) between the two could be observed.

The mixture of BDP-C₆₀ dyad and perylene was excited at 525 nm, corresponding to the absorption of the BDP moiety, under argon saturation at room temperature in toluene. It should be noted that perylene does not absorb at this wavelength. The respective decay and evolution of triplet C₆₀ and triplet perylene was monitored using transient absorption spectroscopy.

Transient absorption spectra of the mixture (**Fig. 6a**) initially show the appearance of the $^3\text{C}_{60}^*$ triplet absorption band at 710 nm as already described in the dyad experiment. The decrease of this band occurs simultaneously with the increase of a new band at around 485 nm, corresponding to the excited state absorption of triplet perylene⁴², suggesting an efficient TTET process from $^3\text{C}_{60}^*$ triplet to the triplet state of perylene. This triplet state absorption band of perylene further decays over longer delay times. Kinetic analyses (**Fig. SI-15**) show a shortened decay time for $^3\text{C}_{60}^*$ at 710 nm ($3.0 \mu\text{s} \pm 0.2 \mu\text{s}$) as compared to that of the dyad alone ($25 \mu\text{s} \pm 3 \mu\text{s}$) in toluene (**Fig. SI-16**), and this decay time is similar to the rising time of the triplet state of perylene at 485 nm, confirming again a TTET process. The triplet perylene further decays with a time constant of (68 ± 7) μs (**Fig. SI-15**).

In order to witness up-converted fluorescence, time-resolved emission of the dyad-perylene mixture was recorded (**Fig. 6b**). Monitoring the emission kinetics at 490 nm gives one rising time constant of (4.0 ± 0.2) μs and one decay time constant of (21 ± 2) μs for the delayed fluorescence of perylene. The rising time is related to the TTET and TTA processes whose kinetics are diffusion-limited. The decay time, which is in the same range as the triplet state lifetime of perylene, corresponds to the TTA process between two triplet molecules⁴³. This lifetime is significantly higher compared to the 3.8 ns reported for perylene alone³⁹ and can unambiguously be assigned to the delayed fluorescence due to TTA up-conversion. **Fig. 7** resumes all the triplet-triplet annihilation processes leading to the delayed fluorescence of perylene.

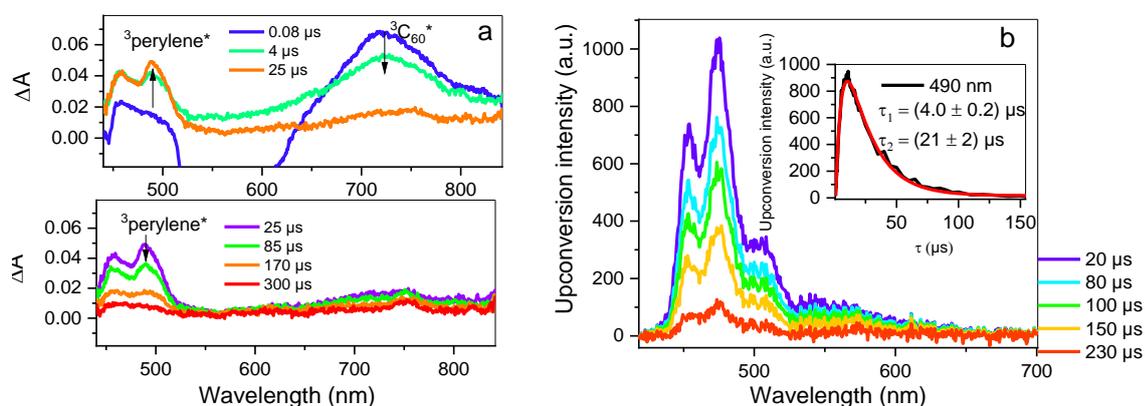


Fig.6. a. Transient absorption spectra and **b.** up-converted fluorescence spectra of BDP-C₆₀ dyad (10 μM) and perylene (400 μM) in deaerated toluene at 525 nm excitation and 40 mW laser power.

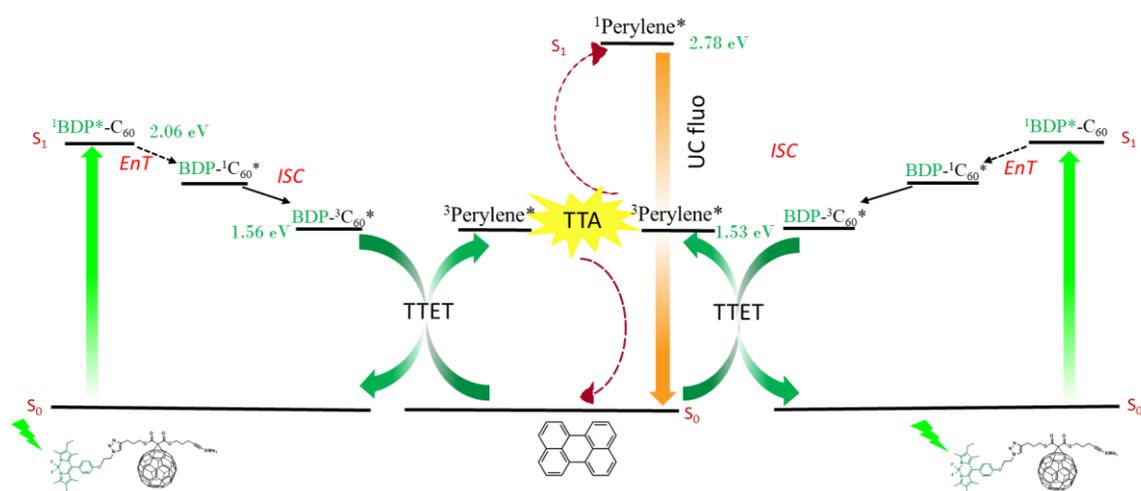


Fig. 7. Scheme of TTA up-conversion in BDP-C₆₀ dyad and perylene. UC fluo: Up-converted fluorescence

A similar experiment was performed with the dyad and triad containing DSBDP with perylene, but no TTET was observed, due to the lower triplet state energy of the DSBDP as compared to that of perylene. In order to evaluate the TTA-UC in the triad, the DSBDP monomer was employed as an annihilator. The triad-DSBDP solution in toluene was excited at 525 nm to attain selective excitation of the BDP unit. Transient absorption spectra of the mixture show the expected formation of ³DSBDP* (**Fig SI-17**), but the lifetime of ³DSBDP* was reduced to $45 \pm 5 \mu\text{s}$ as opposed to $(230 \pm 28) \mu\text{s}$ for the triad alone in toluene (**Fig. SI-18**), implying a TTET/TTA process between ³DSBDP* (triad) and ³DSBDP* (monomer).

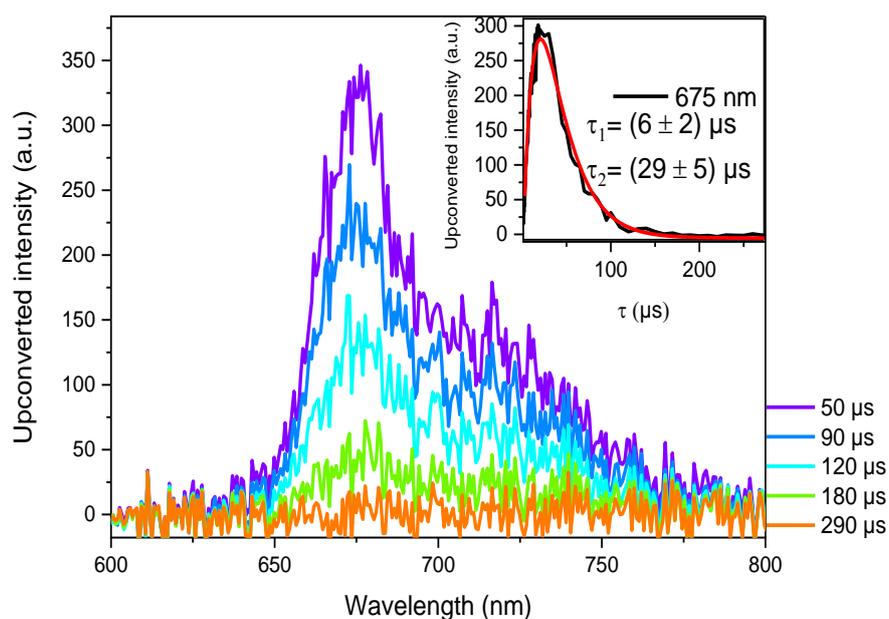


Fig. 8. Up-converted fluorescence spectra of BDP-C₆₀-DSBDP triad (10 μM) and DSBDP-monomer (400 μM) in deaerated toluene at 525 nm excitation and 40 mW laser power. Inset: Decay profile at 675 nm

Further, similarly to the delayed fluorescence observed for perylene, fitting the time resolved fluorescence kinetics at 675 nm corresponding to the emission of ¹DSBDP*, gives one rising time of (6 ± 2) μs and one decay time of (29 ± 5) μs (**Fig. 8**). This long decay time compared to the prompt fluorescence lifetime of the DSBDP monomer (4.46 ns, **Fig. SI-8**) clearly points towards the TTA-UC leading to the delayed fluorescence of DSBDP. Also, control experiments performed on the DSBDP monomer or triad (**Fig. SI-19**) in the same experimental conditions do not reveal any delayed fluorescence. These findings confirm that UC occurred due to indiscernible processes of TTA between ³DSBDP* (triad-monomer) and/or ³DSBDP* (monomer-monomer).

4. Conclusion

We have photophysically studied a novel broadband light-capturing BODIPY-fullerene-based triad and its control dyads, synthesized by a click chemistry approach. The two differently functionalized BODIPY units mounted on the two arms of a C₆₀ core results in an extended UV visible absorption spectrum (300-700 nm), due to the cumulative absorptions of the two BODIPYs. The photophysical properties of the dyads and triad were studied by steady-state and time-resolved emission, as well as nanosecond transient absorption. Excitation of BODIPY chromophores can lead to the formation of a triplet state centered on C₆₀ or the BODIPY moieties depending on the BODIPY structure. In the case of the BDP-C₆₀ dyad, nanosecond transient absorption studies confirm the formation of the triplet excited state of C₆₀, whereas for the DSBDP-C₆₀ and the BDP-C₆₀-DSBDP triad, the triplet excited state centered on the DSBDP moiety was detected. This phenomenon is supported by the lower positioning of the ³DSBDP* energy level as compared to ³C₆₀*. The use of BDP-C₆₀ and BDP-C₆₀-DSBDP as potential organic triplet photosensitizers for triplet-triplet annihilation up-conversion was demonstrated. This work is useful for the development of a new wideband light-capturing, heavy-atom-free organic triplet photosensitizer, with an appreciably long triplet lifetime (280 μs for ³DSBDP*) at room temperature.

Supplementary Information

The online version contains available supplementary material.

Author Contributions

Conceptualization: AF, RMR, MH, TP; investigation: AF, JR, EA, HF, KW, GB, GC and MS; supervision: TP, RMR, KS and MH; writing—original draft preparation: AF, KS and MH; funding acquisition: MH, RMR and TP. All authors have read and agreed to the submitted version of the manuscript.

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Statements and Declarations

On behalf of all authors, the corresponding authors state that there is no conflict of interest.

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