## Photochemical Charge Separation in Closely Positioned Donor–Boron Dipyrrin–Fullerene Triads

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**Abstract:** A series of molecular triads, composed of closely positioned boron dipyrrin–fullerene units, covalently linked to either an electron donor (donor<sup>1</sup>–acceptor<sup>1</sup>–acceptor<sup>2</sup>-type triads) or an energy donor (antenna–donor<sup>1</sup>–acceptor<sup>1</sup>-type triads) was synthesized and photoinduced energy/electron transfer leading to stabilization of the charge-separated state was demonstrated by using femtosecond and nanosecond transient spectroscopic

techniques. The structures of the newly synthesized triads were visualized by DFT calculations, whereas the energies of the excited states were determined from spectral and electrochemical studies. In the case of the antenna–donor<sup>1</sup>– acceptor<sup>1</sup>-type triads, excitation of the

**Keywords:** antenna • electron transfer • energy transfer • fullerenes • photosynthesis antenna moiety results in efficient energy transfer to the boron dipyrrin entity. The singlet-excited boron dipyrrin thus generated, undergoes subsequent energy and electron transfer to fullerene to produce a boron dipyrrin radical cation and a fullerene radical anion as charge-separated species. Stabilization of the charge-separated state in these molecular triads was observed to some extent.

## Introduction

The ability of natural photosynthetic systems to efficiently transform sunlight into chemical energy<sup>[1]</sup> has inspired basic research in artificial photosynthesis<sup>[2–7]</sup> leading to the developments in the areas of photovoltaics and photocatalysis.<sup>[8–10]</sup> The different steps in artificial photosynthesis involve the sequence of wide-band light harvesting and funneling, charge separation and migration, combined with slow charge recombination.<sup>[2–7]</sup> In this regard, the delocalization of charges within the spherical carbon structure of the rigid aromatic  $\pi$  sphere of fullerenes<sup>[11]</sup> offers unique opportunities for stabilizing charge-separated states in donor–acceptor systems.<sup>[4,5,7]</sup> The small reorganization energies of fullerenes

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in electron-transfer reactions have led to advances in synthetic electron donor-acceptor systems capable of performing fast charge separation and relatively slow charge recombination.<sup>[12-14]</sup> Often, electron donors, such as porphyrin, ferrocene (Fc), thiophene, or carbon nanotubes, have been linked to fullerene to create plethora of dyads.<sup>[4,5,7]</sup> Attachment of additional antenna or redox-active molecules resulted in polyads (triads, tetrads, etc.) capable of undergoing sequential energy or electron transfer, or combination of these photochemical processes leading to long-lived charge-separated states. In few studies, the polyads have been utilized to build photovoltaic devices and successful conversion of light into electricity has been demonstrated.<sup>[4]</sup> Such success has lead to further exploration of polyads made out of different donor and acceptor entities capable of harvesting solar energy.<sup>[8,15]</sup>

Recently we reported a new type of donor<sup>1</sup>–acceptor<sup>1</sup>– acceptor<sup>2</sup> triads in which a sensitizer, boron dipyrrin (abbreviated as BDP and also known as BODIPY = borondipyrromethene) was directly linked to an electron donor and an electron acceptor (acceptor<sup>2</sup>).<sup>[16]</sup> The first triad, **1**, was composed of ferrocene–boron dipyrrin—fullerene, whereas the second one, **2**, was made out of triphenylamine–boron dipyrrin–fullerene (Scheme 1). Femtosecond transient absorption studies revealed occurrence of sequential electron transfer in the former ferrocene–boron dipyrrin–fullerene triad, ultimately resulting in stabilization of the charge-separated state. The BDP has so far been used as an antenna molecule (energy donor) as well as an electron donor and an acceptor in the photosynthetic antenna-reaction center mimics and photovoltaic cells.<sup>[17–20]</sup> However, BDP has yet to be utilized

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Scheme 2. Synthetic methodology adopted for the preparation of triads in the present study.

Scheme 1. Structures of the donor<sup>1</sup>-acceptor<sup>1</sup>-acceptor<sup>2</sup> type (1 and 2) and the antenna-donor<sup>1</sup>-acceptor<sup>1</sup> type (3-6) triads investigated in the present study. Dyad 7 and compound 8 are control compounds. For other control compounds see Figure S1 in the Supporting Information.

as both, an energy acceptor and an electron donor, within a supramolecular construct.

We report herein for the first time an extensive series of triads in which the redox active donors in 1 and 2 are replaced by various antenna molecules (compounds 3-6 in Scheme 1, control compounds 3a-6a that were used in the present study, are given in the Supporting Information, Figure S1). Here, BDP acts as both, an energy acceptor and an electron donor. Femtosecond and nanosecond transient absorption studies have been performed to visualize charge stabilization at different time scales in this series of triads.

## **Results and Discussion**

The syntheses of the triads were accomplished, first, by synthesizing the difluoroboron dipyrrin dyads with the desired donor/antenna entity in the *meso* position. The difluoroboron dipyrrin was subsequently converted into dioxyboron dipyrrin derivatives by treatment with dihydroxy benzaldehyde in the presence of AlCl<sub>3</sub> in dry CH<sub>2</sub>Cl<sub>2</sub>. Finally, the electron acceptor was appended by treatment with fullerene and *N*-methylglycine in toluene, according to Scheme 2 (see the Experimental Section for details). The newly synthesized compounds were fully characterized by <sup>1</sup>H NMR spectros-

copy, MALDI-TOF mass spectrometry (Figure S19 in the Supporting Information), electrochemical and other spectroscopic methods as described in the Experimental Section.

**Optical absorption and emission studies**: Figure 1 shows the absorption spectrum of triad **3** and the relevant control compounds in benzonitrile (PhCN). Absorption peaks corre-



Figure 1. Normalized absorption spectra (to the 500 nm band of BDP, except for pyrene butyric acid) of a) triad, **3**, b) dyad, **7**, c) pyrene butyric acid, d) dyad **3a**, and e) **8** in PhCN.

sponding to all of the three entities of the triad are observed and a close examination revealed the following: the pyrene peaks located in the 300–350 nm region reveal 2–3 nm blueshift compared to the control compound (pyrene butyric acid). However, an opposite effect is observed for the BDP

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band located in the 500 nm region, that is, up to 4 nm redshift for the triad compared with the control compound 7, which lacks the antenna entity, and up to 8 nm redshift compared to compound 8, which lacks both pyrene and fullerene entities. The fullerene peak maximum located around  $\lambda =$ 328 nm is overlapped with the pyrene absorption band in the case of triad 3. The observed spectral shift and broadening suggest occurrence of intramolecular interactions between the different entities of the triad. Similar trends in the absorption spectra of triads 4–6 were also observed (see the Supporting Information, Figures S2 a–S4 a), indicating interactions between the different entities of the triads.

Energy transfer from the antenna unit to BDP was observed in the case of dyads 3a-6a (Figure S1), which have covalently connected antenna (pyrene, anthracene, fluorene, or naphthalene) and BDP entities. As shown in Figure 2A,



Figure 2. Fluorescence spectra of A) pyrene butyric acid (a), **3a** (b), **8** (c), **7** (d), and **3** (e) in PhCN excited at  $\lambda = 345$  nm, which corresponds to the pyrene unit. B) Fluorescence spectra of a) **3a**, b) **3**, and c) **7** in PhCN excited at  $\lambda = 506$  nm, which corresponds to the BDP unit. The 600–900 nm region in B) is expanded (×100) to visualize the fullerene emission at  $\lambda = 720$  nm.

excitation of the control compound, pyrene butyric acid, at  $\lambda = 345$  nm revealed emission bands in the 360–430 nm range, corresponding to pyrene singlet emission. When dyad **3a**, possessing pyrene and BDP units, was excited at this wavelength, the emission due to pyrene was quenched over 98% with the concurrent appearance of BDP emission at  $\lambda = 520$  nm. In a control experiment, compound **8** having only BDP but not pyrene unit was excited at  $\lambda = 345$  nm.

Weak emission of BDP, less than 6% of that observed in the case of **3a**, was observed. These observations suggest that the emission band of BDP at  $\lambda = 520$  nm in the case of **3a** is due to efficient energy transfer<sup>[20]</sup> from pyrene to BDP. Similar observations were also made in the case of dyads **4a–6a**, where excitation of the antenna entity resulted in efficient energy transfer to the BDP entity (see Figures S2b– S4b). Interestingly, in the case of triad **3**, excitation at  $\lambda =$ 345 nm, corresponding to the pyrene unit, resulted in no emission of either pyrene or BDP, suggesting additional energy- or electron-transfer processes that involve the fullerene entity.

Figure 2B shows the fluorescence emission behavior of triad 3 and the control compounds when excited at  $\lambda =$ 506 nm, which corresponds to the BDP entity. When compounds **3a** and **8** were excited at  $\lambda = 506$  nm, emission of BDP at  $\lambda = 520$  nm was observed. However, in the case of triad 3 or dyad 7, which have a fullerene as an electron acceptor, the BDP emission was found to be quenched over 99% suggesting efficient photochemical process from singlet-excited BDP to the attached fullerene. This was also the case for triads 4-6, where no emission from either the antenna unit or the BDP unit was observed (see Figures S3c-S5c). The quenching process may involve the energy transfer and/or electron transfer from the singlet BDP to the closely attached  $C_{60}$ , as will discuss later in forthcoming sections. Expanding the scale in the 700-800 nm region revealed weak emission at  $\lambda = 720$  nm corresponding to emission of fulleropyrrolidine. As discussed in the subsequent sections, involving transient absorption studies, this is indeed due to the occurrence of singlet-singlet energy transfers from the BDP (2.38 eV) to  $C_{60}$  (1.75 eV).

Geometry optimization by using DFT calculations: The structures of the triads were visualized by performing computational calculations at the B3LYP/6-31G\* level.<sup>[21]</sup> All of the triads revealed stable structures on the Born-Oppenheimer potential energy surface (Figure 3). In all of the triads the center-to-center distances between the boron atom to the center of fullerene were found to be around 10.3 Å, whereas the center-to-center distances between the donor entity to the boron atom were found to range between 10–11 Å. Additionally, the molecular size, measured between the farthest carbon atoms of the triads, were found to be in the range of 24-26 Å, indicating smaller size for the present triads compared to most of the triads with fullerene as electron acceptor described in literature.<sup>[4,5,7]</sup> The frontier HOMOs and LUMOs were also generated to visualize the electronic structures. In the entire antenna-bearing series of triads, that is 3-6 and the dyad 7, the LUMOs were localized on the fullerene entity, whereas the HOMOs were located on the BDP entity, partially extended to the pyrrolidine nitrogen. These results suggest formation of antenna-BDP<sup>+</sup>-C<sub>60</sub><sup>--</sup> as charge-separated species in the photoinduced electron transfer (PET) reaction.

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Figure 3. Space-filling models of the B3LYP/6-31G\*-optimized structures of the triads 1-6 and the dyad 7. The HOMO and LUMO of triad 3 are also shown in the lower panel.

Electrochemical studies and energy states: Differential pulse voltammetry (DPV) experiments were performed to evaluate the redox potentials. The site of electron transfer corresponding to different entities was determined by performing experiments involving the control compounds, the dyads, and the monomers. For all of the investigated triads, the first reduction corresponding to fullerene was located at -1.03 V versus ferrocene/ferrocenium (Fc/Fc<sup>+</sup>). Additional reductions at -1.43 and -2.05 V were also observed and correspond to the second and third reductions of the fullerene entity. The BDP reduction in 8 was located at -1.63 V, however, in the case of triads 3-6, having covalently linked fullerene units, this process was anodically shifted by 50 mV and occurred at -1.58 V versus Fc/Fc<sup>+</sup> (Figure 4). The oxidation corresponding to ferrocene in 1 was located at 0.05 V, whereas the oxidation corresponding to triphenylamine in 2 was located at 0.61 V versus Fc/Fc<sup>+</sup>. Boron dipyrrin in the



Figure 4. Differential pulse voltammograms of triads **3–6** and **8** in PhCN, 0.1 M tetra-*n*-butylammonium perchlorate ((TBA)ClO<sub>4</sub>). Scan rate =  $5 \text{ mV s}^{-1}$ , pulse width = 0.25 s, pulse height = 0.025 V.

triads revealed oxidation around 0.73 V versus Fc/Fc+, whereas the oxidation of the antenna entities of the triads 3-6 occurred beyond this oxidation process and was often a quasireversible to irreversible process. The slight changes in the redox potentials of the entities in the triads compared to reference 8 is consistent with the earlier-discussed optical absorption data indicating intramolecular interactions. Hence, probable light-induced the charge separation is predicted to occur between the electrondonating BDP and the electron-accepting C60 units, supporting the computational data.

Free-energy calculations for different charge-separated (CS) states were performed according to Equation (1), based on the Weller approach,<sup>[22]</sup>

$$\Delta G_{\rm CS} = E_{\rm ox} - E_{\rm red} - \Delta E_{00} + \Delta G_{\rm S} \tag{1}$$

where  $\Delta E_{00}$  and  $\Delta G_{\rm S}$  correspond to the energy of <sup>1</sup>BDP\* and the electrostatic energy, respectively.  $E_{\rm ox}$  and  $E_{\rm red}$  represent the oxidation potential of the donor and the reduction potential of the acceptor, respectively. On the basis of the first oxidation potential of BDP and the first reduction potential of the C<sub>60</sub> moiety in the triads **3–7**, the driving force for the charge-recombination (CR) process ( $-\Delta G_{\rm CR}$ ) was determined to be 1.71 eV in benzonitrile.<sup>[16]</sup> Considering the energy level of  ${}^{1}C_{60}^{*}$  (1.75 eV), which is very close to that of the charge-separated state in benzonitrile, the eventual charge-separation process, to take place between BDP and C<sub>60</sub>, is expected to be driven by only  ${}^{1}\text{BDP*}$ , possessing an energy value of 2.30 eV. Accordingly,  $\Delta G_{\rm CS}$  was estimated to be 0.67 eV with respect to the  $-\Delta G_{\rm CR}$  value and the energy of the singlet excited state of the BDP chromophore.

As reported earlier, free-energy calculations suggested occurrence of sequential electron transfer resulting in a distant charge-separated state in the case of **1**, and population of low-lying  ${}^{3}C_{60}*$  in the case of **2**.<sup>[16]</sup> For the triads **3–6**, bearing an antenna unit, owing to the higher oxidation potential of the antenna unit than that of BDP and the much lower reduction potential than that of fullerene, an energy level diagram close to that of **2** could be constructed; as shown for triad **3** in Figure 5. That is, excitation of the antenna unit that would undergo energy transfer to the BDP unit, which in turn transfers its electron to the attached C<sub>60</sub> forming the antenna–BDP<sup>++</sup>–C<sub>60</sub><sup>--</sup>. Additionally, the singlet–singlet energy transfer from the BDP to C<sub>60</sub> can also be consid-



Figure 5. Energy-level diagram depicting different photochemical processes of triads **3–6** (X = anthracene, pyrene, 2-naphthalene, or 2-fluorene;  $k_{\rm T}$  = decay constant).

ered.<sup>[23,24]</sup> The finding that the energy level of pyrene– BDP<sup>++</sup>– $C_{60}^{-}$  is comparable to that of the singlet state of  $C_{60}$ suggests that electron transfer through the  ${}^{1}C_{60}^{*}$  is thermodynamically unfavorable. In any case, because the energy level of the triplet state of fullerene is the lowest, population of  ${}^{3}C_{60}^{*}$  prior to the formation of the ground state species could be rationalized from these studies. The forthcoming section discusses these photochemical events in detail.

**Transient absorption studies**: Femtosecond and nanosecond transient spectral measurements were performed to identify the electron-transfer products, the mechanistic details of charge migration, and the kinetics of charge-separation and charge-recombination processes. Nanosecond transient differential absorption spectra of tolyIBDP (8) excited at  $\lambda = 510$  nm showed weak absorbance on either side of the bleaching signal, which were assigned to the triplet excited state of BDP (see Figure S5 in the Supporting Information).<sup>[25]</sup> The time profile of tolyIBDP at  $\lambda = 400$  nm confirms a long-lived triplet state of about 45 µs. Excitation at  $\lambda = 355$  nm gave the same transient spectrum of the triplet state of tolyIBDP. Typically, triplet formation of BDP dyes is remarkably inefficient.<sup>[26]</sup>

Femtosecond measurements of dyad **1a** in PhCN by using  $\lambda = 460$  nm as excitation wavelength, which selectively excites the BDP entity, resulted in electron transfer from the Fc to the attached BDP forming Fc<sup>+</sup>-BDP<sup>-.[15]</sup> The nanosecond transient spectra of dyad **1a** lacked absorption bands of triplet state BDP due to the occurrence of CR to the low-lying triplet state of the Fc entity. Interestingly, upon photoexcitation of the BDP entity of triad **1** in deaerated PhCN, the characteristic absorption bands of BDP<sup>--</sup> were observed at early time scale ( $\approx 1$  ps), however, at longer time scale, the band corresponding to BDP<sup>--</sup> at  $\lambda = 590$  nm decreased in intensity with concurrent build-up of the absorption band of C<sub>60</sub><sup>--</sup> at  $\lambda = 1000$  nm, suggesting an electron

shift from BDP<sup>--</sup> to the attached C<sub>60</sub> entity and formation of Fc<sup>+-</sup>-BDP-C<sub>60</sub><sup>--</sup> as the final CS state. The rate constant of the charge shift from BDP<sup>--</sup> to C<sub>60</sub> was determined to be  $3.8 \times 10^{11} \text{ s}^{-1}$ . By following the decay of Fc<sup>+-</sup>-BDP-C<sub>60</sub><sup>--</sup> in PhCN, the CR rate constant was determined to be  $2.4 \times 10^9 \text{ s}^{-1}$ , from which a lifetime of 420 ps for the radical-ion pair (RIP) was derived. The finding that the  $\tau_{\text{RIP}}$  of Fc<sup>+-</sup>-BDP-C<sub>60</sub><sup>--</sup> is much longer than that of Fc<sup>+-</sup>-BDP<sup>--</sup> ( $k_{\text{CR}} = 5.8 \times 10^{10} \text{ s}^{-1}$ ;  $\tau_{\text{RIP}} = 17 \text{ ps}$ ) revealed the effect of the electron shift mechanism in prolonging the  $\tau_{\text{RIP}}$  in triad **1**. That is, as a result of relatively distant positioning of the radical cation and anion, stabilization of the charge-separated state is accomplished in triad **1** in spite of closely disposed donor and acceptor entities.

Photoirradiation of triad **2** revealed the characteristic absorption band of  $C_{60}^{-}$  in the near IR region with a maximum at  $\lambda_{CS} = 1000$  nm.<sup>[5]</sup> The absorption band of TPA<sup>++</sup> was not observed suggesting that the formation of  $C_{60}^{-}$  results from electron transfer from the singlet-excited BDP as an electron donor to  $C_{60}$ . A hole transfer from TPA to BDP<sup>++</sup> is slightly exergonic (<0.1 eV), however, the lack of a TPA<sup>++</sup> band suggests this process to be less efficient. The  $k_{CR}$  value of TPA-BDP<sup>++</sup>-C<sub>60</sub><sup>--</sup> was determined to be 2.0× 10<sup>9</sup> s<sup>-1</sup>, from which a  $\tau_{RIP}$  value of 500 ps was evaluated. At longer time scale (1800 ps), the spectrum revealed the characteristic absorption of the triplet  $C_{60}$  suggesting that the radical-ion pair decays through CR to populate the triplet  $C_{60}$ .

The tolylBDP–C<sub>60</sub> dyad (7) revealed transient spectral traits in which peak formation at  $\lambda = 1000$  nm, as a fingerprint of the radical anion of C<sub>60</sub> (Figure 6),<sup>[27,28]</sup> declares that charge separation occurs between tolylBDP and C<sub>60</sub>. The broadening in the absorption band in the near IR region may suggest a contribution of an energy transfer from singlet BDP to singlet C<sub>60</sub> in the quenching process. Formation of the charge-separated state within a few picoseconds is probably achieved due to the close proximity of electron donor and electron acceptor moieties. Considering this proximity, charge separation prior to energy transfer between



Figure 6. Femtosecond transient absorption spectra obtained by 460 nm laser excitation of tolyIBDP-C<sub>60</sub> (7) in deaerated PhCN (black=45, green=130, pink=360, and blue=2500 ps). The inset shows the time profile of C<sub>60</sub><sup>--</sup> at  $\lambda$ =1000 nm.

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tolyIBDP and C<sub>60</sub> is also possible (Figure S6 in the Supporting Information). The rate constant of charge recombination was determined from the first-order decay at  $\lambda_{\rm CS} = 1000$  nm to be  $3.2 \times 10^9$  s<sup>-1</sup>, corresponding to a lifetime ( $\tau_{\rm CS}$ ) of 310 ps. The quantum yield of charge separation<sup>[7e]</sup> was determined from the quenching of the singlet excited state of C<sub>60</sub> to be 0.87.

In the complementary nanosecond transient absorption spectral measurements (Figure 7 and Figure 86 in the Sup-



Figure 7. Nanosecond transient absorption spectra of tolylBDP– $C_{60}$  (7) in PhCN,  $\lambda_{ex} = 510$  nm (black = 1, dark green = 12, pink = 20, light green = 28, purple = 40, and blue = 90 µs). The inset shows the time profile of  ${}^{3}C_{60}^{*}$  at  $\lambda = 700$  nm.

porting Information), only the characteristic triplet-state spectrum of  $C_{60}$  was observed at  $\lambda = 700 \text{ nm}$ ,<sup>[29,30]</sup> when excited with 510 nm laser pulses at which the tolylBDP is excited dominantly (Figure 7). The formation of triplet  $C_{60}$  is most likely due to the charge recombination of BDP<sup>++</sup>- $C_{60}^{--}$ , taking into account that the energy level of triplet  $C_{60}$  (1.55 eV) is located lower than that of BDP<sup>++</sup>- $C_{60}^{--}$ . The triplet–triplet energy transfer from tolylBDP to  $C_{60}$  was ruled out due to the lack of transient spectral features of the triplet excited state of tolylBDP. The decay rate constant of tolylBDP– $^{-3}C_{60}^{+*}$  to the ground state was found to be  $4.3 \times 10^4 \text{ s}^{-1}$ .

The intramolecular photoinduced processes of **7** are compiled in a energy level diagram (see Figure S7 in the Supporting Information). Excitation of the tolyIBDP chromophore results in electron transfer/energy transfer to the singlet excited state of  $C_{60}$ . The formed charge-separated state undergoes charge recombination to produce the triplet state of  $C_{60}$ . Then, it decays to the ground state within 24 µs.

The femtosecond transient absorption difference spectra of triad **3** exhibited quite the same characteristics as those of tolylBDP–C<sub>60</sub> except for the rate constant of charge recombination ( $k_{CR}=1.3\times10^9$  s<sup>-1</sup>), figured through the monoexponential decay at  $\lambda = 1020$  nm, coinciding a CS lifetime of 770 ps (Figure 8). Fast charge separation within a few picoseconds is also favored in this triad, thereby enhancing the formation of the triplet excited state of C<sub>60</sub>. As expected, the nanosecond transient spectra of triad **3** (Figure 9) con-



Figure 8. Femtosecond transient absorption spectra obtained by 460 nm laser excitation of pyrene–BDP– $C_{60}$  (3) in deaerated PhCN (black = 360. pink = 880, and blue = 2900 ps). The inset shows the decay time profile of  $C_{60}^{--}$  at  $\lambda = 1000$  nm.



Figure 9. Nanosecond transient absorption spectra of pyrene–BDP– $C_{60}$ (3) in PhCN,  $\lambda_{ex}$ =510 nm (black=1, yellow=5, red=15. green=30, and blue=85 µs). The inset shows the time profile of  ${}^{3}C_{60}^{*}$  at  $\lambda$ =700 nm.

firm the formation of the triplet excited state of C<sub>60</sub> with the same decay constant ( $k_{\rm T} = 4.1 \times 10^4 \, {\rm s}^{-1}$ ,  $\tau_{\rm T} = 24 \, \mu {\rm s}$  at 700 nm). In a control experiment, the nanosecond transient spectra of dyad 3a showed weak absorption bands in the visible region with maxima at  $\lambda = 430$  and 630 nm that correspond to the triplet formation of BDP (see Figure S8 in the Supporting Information). As depicted in Figure 5 for the photoinduced intramolecular processes of triad 3 in benzonitrile, the 345 nm laser excitation pumps up the pyrene moiety to its singlet excited state, from which the energy transfer from the singlet pyrene to the attached BDP takes place quite efficiently, as confirmed by steady-state emission studies. From the time-resolved emission measurements, the chargeseparation process from the singlet BDP to the C<sub>60</sub> was recorded. The charge-separated state recombined to populate the triplet C<sub>60</sub>, but not the triplet BDP, as evidenced from the nanosecond transient absorption measurements.

The triads bearing anthracene, fluorene, and naphthalene moieties, that is **4–6**, revealed similar antenna effects. The femtosecond transient absorption spectra of each triad had the same spectral patterns expressing the formation of the charge-separated states between the BDP moiety and the

# $C_{60}$ unit with different lifetimes when excited at $\lambda = 460$ nm (see Figure S9–S11 in the Supporting Information). Nanosecond transient absorption spectra of each triad system confirmed formation of the triplet excited state of $C_{60}$ when laser pulses were utilized at $\lambda = 510$ and 355 nm (see Figure S12–S18 in the Supporting Information). The lifetimes of the charge-separated states are compiled in Table 1. Be-

Table 1. Lifetimes of the charge-separated state in the series of triads and dyad investigated in the present study.

Compound	$k_{ m CR}{}^{[a]}  [{ m s}^{-1}]$	$ au_{\rm CS}^{[a]}$ [ps]
$Fc-BDP-C_{60}$ (1)	$2.4 \times 10^{9}$	420
TPA—BDP– $C_{60}$ (2)	$2.0 \times 10^{9}$	500
pyrene—BDP– $C_{60}$ (3)	$1.3 \times 10^{9}$	770
anthracene—BDP– $C_{60}$ (4)	$1.1 \times 10^{9}$	900
fluorene—BDP– $C_{60}$ (5)	$2.6 \times 10^{9}$	390
naphthalene—BDP– $C_{60}$ (6)	$1.3 \times 10^{9}$	770
tolylBDP– $C_{60}$ (7)	$3.2 \times 10^{9}$	310

[a] The experimental error is  $\pm 5$  %.

sides functioning as antenna units in triad systems, anthracene, pyrene, fluorene, and naphthalene entities appear to affect the lifetimes of the charge-separated states to some extent, even though they are not directly involve in a charge migration as electron donor moieties as understood from the earlier-discussed results that were gained in electrochemical measurements.

#### Conclusion

A series of molecular triads with closely spaced different entities, comprising of BDP and fullerene primary entities, and a third entity, either a redox-active or an antenna entity, was synthesized to examine the photodynamic properties. The optical absorption studies revealed intramolecular interactions between the entities of the triads. The geometry and electronic structure of the triads were deduced from computational studies, whereas electrochemical studies by using differential pulse voltammetry technique allowed establishing energy states of the different triads. Fluorescence studies revealed efficient energy transfer from the antenna entity to the boron dipyrrin entity in triads **3–6**. The <sup>1</sup>BDP\* transfers its electron to the attached C<sub>60</sub>, thereby generating antenna-BDP<sup>++</sup>– $C_{60}^{-}$  charge-separated species, as revealed by femtosecond and nanosecond transient absorption techniques. The anticipated stabilization of the charge-separated state was observed to some extent in all investigated triads.

#### **Experimental Section**

**Chemicals**: All of the reagents used in the syntheses, and benzonitrile (in sure seal bottle under nitrogen) were obtained from Aldrich Chemicals (Milwaukee). Tetra-*n*-butylammonium perchlorate, (TBA)ClO<sub>4</sub>, was obtained from Fluka Chemicals. All the chromatographic materials and solvents were procured from Fisher Scientific and were used as received. The syntheses and purification of **1**, **2**, and **8** are given elsewhere.<sup>[16]</sup>

Instruments: The UV/Vis spectral measurements were carried out with a Shimadzu Model 1600 UV/Vis spectrophotometer. The fluorescence emission was monitored by using a Varian Eclipse spectrometer. A right angle detection method was used. The <sup>1</sup>H NMR studies were carried out on a Varian 400 MHz spectrometer. Tetramethylsilane (TMS) was used as an internal standard. Differential pulse voltammograms were recorded on an EG&G PARSTAT electrochemical analyzer with a three electrode system. A platinum button electrode was used as the working electrode. A platinum wire served as the counter electrode and an Ag/AgCl electrode was used as the reference electrode. The ferrocene/ferrocenium redox couple was used as an internal standard. All the solutions were purged prior to electrochemical and spectral measurements with argon gas. Matrix-assisted laser desorption/ionization time-of-flight mass spectra (MALDI-TOF MS) were measured on a Kratos Compact MALDI I (Shimadzu) for metal complex in PhCN with dithranol used as a matrix. The computational calculations were performed by DFT B3LYP/6-31G\* methods with the Gaussian 03 software package<sup>[21]</sup> on high-speed PCs. The HOMOs and LUMOs were generated by using the GaussView program<sup>[31]</sup>.

Laser flash photolysis: The studied compounds were excited by a Panther OPO pumped by Nd/YAG laser (Continuum, SLII-10, 4-6 ns fwhm) with the powers of 1.5 and 3.0 mJ per pulse. The transient absorption measurements were performed by using a continuous xenon lamp (150 W) and an InGaAs-PIN photodiode (Hamamatsu 2949) as a probe light and a detector, respectively. The output from the photodiodes and a photomultiplier tube was recorded with a digitizing oscilloscope (Tektronix, TDS3032, 300 MHz). Femtosecond transient absorption spectroscopy experiments were conducted by using an ultrafast source: Integra-C (Quantronix Corp.), an optical parametric amplifier: TOPAS (Light Conversion Ltd.), and a commercially available optical detection system: Helios provided by Ultrafast Systems LLC. The source for the pump and probe pulses were derived from the fundamental output of Integra-C (780 nm, 2 mJ per pulse and fwhm = 130 fs) at a repetition rate of 1 kHz; 75% of the fundamental output of the laser was introduced into TOPAS, which has optical frequency mixers resulting in tunable range from 285-1660 nm, whereas the rest of the output was used for white-light generation. Typically, 2500 excitation pulses were averaged for five seconds to obtain the transient spectrum at a set delay time. Kinetic traces at appropriate wavelengths were assembled from the time-resolved spectral data. All measurements were conducted at 298 K. The transient spectra were recorded by using fresh solutions in each laser excitation.

General procedure for synthesis of aryl difluoroboron dipyrrin: The aryl difluoroboron dipyrrin compounds were synthesized according to the procedure described by Imahori et al.<sup>[18a]</sup> with some modifications. Trifluoroacetic acid (0.19 mL, 2.47 mmol) was added to a mixture of aryl aldehyde (12.4 mmol) and 2,4-dimethylpyrrole (2.16 mL, 21.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (800 mL). The reaction mixture was stirred at room temperature under argon. After 1.5 h the resulting solution was washed with aqueous NaOH (0.1 M, 200 mL) and water (200 mL). The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent was evaporated under reduced pressure. The residue was dissolved in toluene (50 mL) and p-chloranil (2.73 g, 11.1 mmol) was added. After 10 min Et<sub>3</sub>N (8 mL) was added followed by BF3. Et2O (7 mL). The mixture was stirred for 1.5 h and then poured into water. The organic layer was extracted with CH2Cl2, dried over anhydrous Na2SO4, and the solvent was evaporated under reduced pressure. The crude product was purified with column chromatography by using mixtures of CH<sub>2</sub>Cl<sub>2</sub> and hexane as eluent.

**1-Pyrene difluoroboron dipyrrin (3a)**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ = 8.29–7.85 (m, 9H; pyrenyl-H), 5.99 (s, 2H; pyrrole-H), 2.6 (s, 6H; CH<sub>3</sub>), 2.41 (s, 6H; CH<sub>3</sub>), 0.85 ppm (s, 6H; CH<sub>3</sub>).

**9-Anthracene difluoroboron dipyrrin (4a):** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ =8.5 (s, 1H; aryl-H), 8.0 (d, *J*=8.30 Hz, 2H; aryl-H), 7.84 (d, *J*=8.47 Hz, 2H; aryl-H), 7.51–7.38 (m, 4H; aryl-H), 5.85 (s, 2H; pyrrole-H), 2.6 (s, 6H;CH<sub>3</sub>), 0.8 ppm (s, 6H; CH<sub>3</sub>).

**2-Fluorene difluoroboron dipyrrin (5a):** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ = 7.92–7.82 (m, 2H; aryl-H), 7.61–7.59 (m, 1H; aryl-H), 7.47–7.28 (m, 6H; aryl-H & dioxyaryl-H), 5.99 (s, 2H; pyrrole-H), 3.99 (s, 2H; fluorenyl-H), 2.59 (s, 6H; CH<sub>3</sub>), 1.4 ppm (s, 6H; CH<sub>3</sub>).

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**2-Napthalene difluoroboron dipyrrin (6a):** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ =8.02–7.75- (m, 4H; aryl-H), 7.58–7.52 (m, 3H; aryl-H), 7.38–7.34 (m, 1H; aryl-H), 6.0 (s, 2H; pyrrole-H), 2.6 (s, 6H; CH<sub>3</sub>), 1.3 ppm (s, 6H; CH<sub>3</sub>).

*p*-Tolyl difluoroboron dipyrrin (7a): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ = 7.28 (d, J=8.54 Hz, 2H; aryl-H), 7.14 (d, J=8.19 Hz, 2H; aryl-H), 5.99 (s, 2H; pyrrole-H), 2.55 (s, 6H; CH<sub>3</sub>), 2.41 (s, 3H; CH<sub>3</sub>), 1.41 ppm (s, 6H; CH<sub>3</sub>).

General procedure for synthesis of aryl-dioxyboron dipyrrin: These compounds were prepared according to the literature procedure with few modifications.<sup>[29]</sup> Aryl difluoroboron dipyrrin (0.730 mmol) was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and stirred under argon for 10 min. Then AlCl<sub>3</sub> (146 mg, 1.096 mmol) was added and the solution was further stirred for 15 min before addition of 3,4-dihydroxybenzaldehyde (151.4 mg, 1.096 mmol). The mixture was stirred for 20 min and the solvent was evaporated under reduced pressure. The crude product was purified by using a deactivated basic alumina column to give the desired compound.

**1-Pyrene-dioxyboron dipyrrin (3b)**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.80 (s, 1 H; aldehyde-H), 8.29–7.85 (m, 9 H; pyrenyl-H), 7.4–7.3 (m, 2 H; dioxyaryl -H), 6.88 (d, 1 H; dioxyaryl-H), 5.99 (s, 2 H; pyrrole-H), 2.1 (s, 6 H; CH<sub>3</sub>), 0.8 ppm (s, 3 H; CH<sub>3</sub>).

**9-Anthracene-dioxyboron dipyrrin (4b)**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ =9.80 (s, 1H; aldehyde-H), 8.5 (s, 1H; aryl-H), 8.0 (d, *J*=8.08 Hz, 2H; aryl-H), 7.84 (d, *J*=8.65 Hz, 2H; aryl-H), 7.58–7.39 (m, 6H; aryl-H & dioxyaryl-H), 6.95 (d, *J*=7.71 Hz, 1H; dioxyaryl-H), 5.9 (s, 2H; pyrrole-H), 2.1 (s, 6H; CH<sub>3</sub>), 0.82 ppm (s, 6H; CH<sub>3</sub>).

**2-Fluorene-dioxyboron dipyrrin (5b)**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.80 (s, 1H; aldehyde-H), 7.92–7.82 (m, 2H; aryl-H), 7.61–7.59 (m, 1H; aryl-H), 7.47–7.28 (m, 6H; aryl-H & dioxyaryl-H), 6.88 (d, *J* = 8.22 Hz, 1H; dioxyaryl-H) 5.99 (s, 2H; pyrrole-H), 3.99 (s, 2H; fluorenyl-H), 2.0 (s, 6H; CH<sub>3</sub>), 1.39 ppm (s, 6H; CH<sub>3</sub>).

**2-Napthalene-dioxyboron dipyrrin (6b):** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 9.80$  (s, 1H; aldehyde-H), 8.02–7.79 (m, 4H; aryl-H), 7.60–7.52 (m, 3H; aryl-H), 7.42–7.34 (m, 3H; aryl-H & dioxyaryl-H), 6.88 (d, J = 8.15 Hz, 1H; dioxyaryl-H) 5.99 (s, 2H; pyrrole-H), 2.05 (s, 6H; CH<sub>3</sub>), 1.32 ppm (s, 6H; CH<sub>3</sub>).

*p*-Tolyl-dioxyboron dipyrrin (7b): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.80 (s,1H; aldehyde-H), 7.36–7.38 (dd, *J* = 7.88, 7.75 Hz, 1H; dioxyaryl-H), 7.33–7.27 (m, 3H; dioxyaryl and aryl-H), 7.14 (d, *J* = 8.60 Hz, 2H; aryl-H), 6.88 (d, *J* = 7.78 Hz, 1H; dioxyaryl-H), 5.99 (s, 2H; pyrrole-H), 2.41 (s,3H; CH<sub>3</sub>), 2.0 (s, 6H; CH<sub>3</sub>), 1.59 (s, 3H; CH<sub>3</sub>), 1.39 ppm (s, 3H; CH<sub>3</sub>).

General procedure for synthesis of aryl-dioxyboron dipyrrin-fullerene triads: The title compounds were synthesized according to the general procedure described by Prato and coworkers for fulleropyrrolidines<sup>[30]</sup> with few modifications. Fullerene C<sub>60</sub> (147 mg, 0.204 mmol), aryl-dioxyboron dipyrrin (0.613 mmol) and *N*-methylglycine (36.4 mg, 0.409 mmol) were dissolved in dry toluene (150 mL). The mixture was heated to reflux for 6 h. The solvent was evaporated under reduced pressure. The crude product was purified by using column chromatography. It may be mentioned here that the triads exist as a mixture of two atropisomers in fast equilibrium.<sup>[32]</sup>

**1-Pyrene-dioxyboron dipyrrin-fullerene triad (3):** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 8.29-7.85$  (m, 9H; pyrenyl-H), 7.4–7.3 (m, 2H; dioxyaryl-H), 6.85 (brs, 1H; dioxyaryl-H), 5.89 (brs, 2H; pyrrole-H), 4.99 (d, J = 9.50 Hz, 1H; fulleropyrrolidine- H), 4.89 (s, 1H; fulleropyrrolidine-H), 4.25 (d, J = 9.70 Hz, 1H; fulleropyrrolidine-H), 2.91 (s, 3H; fulleropyrrolidine-H), 0.81 ppm (s, 12H; CH<sub>3</sub>); MS (MALDI-TOF): m/z calcd for C<sub>104</sub>H<sub>38</sub>BN<sub>3</sub>O<sub>2</sub>: 1296.11; found: 1294.4.

**9-Anthracene-dioxyboron dipyrrin-fullerene triad (4):** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ =8.5 (s,1H; aryl-H), 8.0 (d, *J*=8.55 Hz, 2H; aryl-H), 7.84 (d, *J*=8.55 Hz, 2H; aryl-H), 7.58–7.39 (m, 6H; aryl-H & dioxyaryl-H), 6.75 (brs, 1H; dioxyaryl-H), 5.9 (brs, 2H; pyrrole-H), 4.99 (d, *J*=9.61 Hz, 1H; fulleropyrrolidine- H), 4.89 (s, 1H; fulleropyrrolidine-H), 4.26 (d, *J*=9.44 Hz, 1H; fulleropyrrolidine-H), 3.5 (s, 1H; fulleropyrrolidine-H), 2.91 (s, 3H; fulleropyrrolidine-H), 1.21 ppm (s, 12H; CH<sub>3</sub>); MS (MALDI-TOF): *m/z* calcd for C<sub>96</sub>H<sub>34</sub>BN<sub>3</sub>O<sub>2</sub>: 1270.07; found: 1269.5.

**2-Fluorene-dioxyboron dipyrrin–fullerene triad (5)**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ =7.92–7.82 (m, 2H; aryl-H), 7.61–7.59 (m, 1H; aryl-H), 7.4–7.28 (m, 6H; aryl-H & dioxyaryl-H), 6.76 (brs, 1H; dioxyaryl-H), 5.9 (brs, 2H; pyrrole-H), 4.99 (d, *J*=9.42 Hz, 1H; fulleropyrrolidine-H), 4.89 (s, 1H; fulleropyrrolidine-H), 4.26 (d, *J*=9.56 Hz, 1H; fulleropyrrolidine-H), 3.99 (s, 2H; fluorenyl-H), 2.91 (s, 3H; fulleropyrrolidine-H), 1.25 ppm (s, 12H; CH<sub>3</sub>); MS (MALDI-TOF): *m*/*z* calcd for C<sub>95</sub>H<sub>34</sub>BN<sub>3</sub>O<sub>2</sub>: 1258.06; found: 1258.8.

**2-Napthalene-dioxyboron dipyrrin-fullerene triad (6):** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ =8.02–7.79-(m, 4H; aryl-H), 7.60–7.52 (m, 3H; aryl-H), 7.42–7.34 (m, 3H; aryl-H & dioxyaryl-H), 6.75 (brs, 1H; dioxyaryl-H), 5.9 (brs, 2H; pyrrole-H), 4.99 (d, *J*=9.45 Hz, 1H; fulleropyrrolidine- H), 4.85 (s, 1H; fulleropyrrolidine-H), 4.22 (d, *J*=9.41 Hz, 1H; fulleropyrrolidine-H), 2.85 (s, 3H; fulleropyrrolidine-H), 1.24 ppm (s, 12H; CH<sub>3</sub>); MS (MALDI-TOF): *m/z* calcd for C<sub>92</sub>H<sub>32</sub>BN<sub>3</sub>O<sub>2</sub>: 1220.01; found: 1219.8.

*p*-Tolyl-dioxyboron dipyrrin–fullerene triad (7): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.40–7.38 (m, 1H; dioxyaryl-H), 7.30–7.22- (m, 1H; dioxyaryl-H), 7.10-7.18 (m, 4H, aryl-H), 6.75 (brs, 1H; dioxyaryl-H), 5.9 (brs, 2H; pyrrole-H), 4.99 (d, *J* = 9.32 Hz, 1H; fulleropyrrolidine-H), 4.89 (s, 1H; fulleropyrrolidine-H), 4.26 (d, *J* = 9.40 Hz, 1H; fulleropyrrolidine-H), 2.91 (s, 3H; fulleropyrrolidine-H), 2.44 (s, 3H; CH<sub>3</sub>), 2.39 (s, 3H; CH<sub>3</sub>), 1.59 (s, 3H; CH<sub>3</sub>), 1.38 (s, 3H; CH<sub>3</sub>), 1.21 ppm (s, 3H; CH<sub>3</sub>); MS (MALDI-TOF): *m/z* calcd for C<sub>89</sub>H<sub>32</sub>BN<sub>3</sub>O<sub>2</sub>: 1183.98; found: 1184.3.

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