Charge stabilization in a closely spaced ferrocene-boron dipyrrin-fullerene triad[†]

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New molecular triads composed of closely spaced ferroceneboron dipyrrin-fullerene, 1 and triphenylamine-boron dipyrrinfullerene, 2 are synthesized, and photoinduced electron transfer leading to charge stabilization is demonstrated using a femtosecond transient spectroscopic technique.

Photoinduced electron transfer is one of the most fundamental and extensively investigated reactions.^{1,2} Its importance in photosynthesis and in the development of energy harvesting devices³ has inspired the design and study of several elegant model systems that made possible to probe the often complex multistep electron-transfer processes.^{1–3} The boron dipyrrin, also known as BODIPY, has frequently been used as an energy absorbing and transferring antenna molecule in the photosynthetic antenna-reaction center mimic as well as a photosensitizer in chemosensor and fluorescent tags.^{4,5} BODIPY can also acts as both an electron donor and an acceptor.⁶ However, BODIPY has yet to be utilized to construct photosynthetic reaction center models that undergo multi-step photoinduced electron-transfer processes.

We report herein two new type of triads in which the BODIPY is either directly linked or having a smaller spacer group with electron donor and acceptor. The structures of these triads are shown in Chart 1. The first triad, **1** is composed of ferrocene-boron dipyrrin-fullerene while the second one, **2** is made out of triphenylamine-boron dipyrrinfullerene. As demonstrated here, femtosecond transient absorption studies reveal occurrence of sequential electron transfer in triad **1** ultimately resulting in charge stabilization.

The syntheses of the triads, **1** and **2** are accomplished, first, by synthesizing *meso*-phenylferrocene or *meso*-triphenylamine substituted difluoroboron dipyrrin dyads. The difluoroboron dipyrrin was subsequently converted into dioxyboron dipyrrin derivatives **1a** and **1b** by treating with dihydroxy benzaldehyde in the presence of AlCl₃ in dry CH₂Cl₂.⁷ Finally, the electron acceptor was appended by reacting with fullerene and

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Chart 1 Structures of the ferrocene-boron dipyrrin-fullerene, 1 and triphenylamine-boron dipyrrin-fullerene 2 triads investigated in the present study. Compounds 1a, 2a and 1b are control compounds.

N-methylglycine in toluene⁸ (see ESI† for synthetic and experimental details). The newly synthesized compounds were fully characterized by ¹H and ¹³C NMR, mass and other spectroscopic methods (see Fig. S1 and S2, ESI,†for ¹H NMR spectra).

Fig. 1(a) and (b) show the optical absorption spectra of the triads 1 and 2 along with their dyad analogs, 1a and 2a having no fullerene entity. The ferrocene entity in 1a shows a band at 326 nm while the triphenylamine entity in 2a revealed an absorption band around 311 nm. The boron dipyrrin entity in both dyads revealed aborption maximum at 504 nm. Upon appending fullerene to form the triads, the band maxima



Fig. 1 Optical absorption and fluorescence emission of 1 and 2 and the reference compounds in PhCN.

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(a)

of (a) 1 and (b) 2 triads.

corresponding to the boron dipyrrin revealed a small red shift of 5 nm, suggesting intramolecular interactions. The 433 nm sharp band of fulleropyrrolidine was also evident for both triads. The dyads, **1a** and **2a**, revealed emission of the boron dipyrrin entity at 519 nm, however, with substantially diminished intensity as compared with the control compound, **1c** suggesting occurrence of intramolecular events in the dyads. Interestingly, the fluorescence emission of boron dipyrrin in the triads was virtually absent (<1%) indicating additional photochemical events.

The structure of the triads were visualized by performing computational calculations at the B3LYP/6-31G* level.⁹ Both triads revealed stable structures on the Born–Oppenheimer potential energy surface (Fig. 2). For **1**, the center-to-center distances between ferrocene iron to the boron atom, and boron to center of fullerene were found to be 10.28 and 10.36 Å, respectively. Similarly, for **2**, the center-to-center distances between triphenylamine nitrogen to boron atom of boron dipyrrin, and boron to center of fullerene were found to be 8.77 and 10.23 Å, respectively. Additionally, the molecular size, measured between the farthest C-atoms of the triads, were found to be 25.5 and 24.9 Å, respectively, for **1** and **2** indicating smaller size for the present triads compared to most of the triads with fullerene as electron acceptor in literature.^{1,2}

Differential pulse voltammetry (DPV) experiments (Fig. 3) were performed to evaluate the redox potentials. The site of electron transfer corresponding to different entities was arrived by performing experiments involving the control compounds, the dyads and the monomers. For both 1 and 2, the first reduction corresponding to fullerene was located at $-1.03 \text{ V} vs. \text{ Fc/Fc}^+$. Further reductions at -1.43, -1.61 and -2.05 V were also observed corresponding to the reductions of fullerene and boron dipyrrin entities. The oxidation corresponding to ferrocene in 1 was located at 0.05 V while that corresponding to triphenylamine in 2 was located at $0.61 \text{ V} vs. \text{ Fc/Fc}^+$. Boron dipyrrin in 1 and 2, revealed

(b)





Fig. 3 Differential pulse voltammograms (DPV) of (i) **1** and (ii) **2** in PhCN, 0.1 M (TBA)ClO₄. Scan rate = 5 mV s^{-1} , pulse width = 0.25 s, pulse height = 0.025 V.

oxidation around 0.74 V vs. Fc/Fc⁺. Free-energy calculations for different charge-separated (CS) states were performed according to Weller approach.¹⁰ Such calculations revealed energy levels for Fc⁺–BDP^{•–}–C₆₀ and Fc⁺–BDP–C₆₀^{•–} to be 1.60 and 1.10 eV, respectively. Similar calculations for **2** yielded energy levels for TPA–BDP^{•+}–C₆₀^{•–} to be 1.77 eV higher than that of TPA–BDP–³C₆₀* (1.53 eV) (see Fig. S5 and S8 in ESI[‡] for energy level diagrams). That is, occurrence of sequential electron transfer resulting in distant CS state in the case of **1** and population of low lying ³C₆₀* in the case of **2** was visualized from these studies.

Femtosecond and nanosecond transient spectral measurements were performed to identify the electron-transfer products, mechanistic details of charge migration, and kinetics of CS and CR processes. The femtosecond measurements of dyad 1a in PhCN by using 460 nm radiation, which selectively excites the BDP entity, showed absorption band at 590 corresponding to the boron dipyrrin radical anion (Fig. 4).¹¹ The ferrocenium cation could not be observed due to its extremely low extinction coefficient (ε). These observations suggest occurrence of electron transfer from the Fc to the attached BDP forming $Fc^{\bullet +}-BDP^{\bullet -}$. Additionally, the nanosecond transient spectra of dvad 1a in deaerated PhCN did not show the absorption bands of triplet BDP. Because the energy level of the $Fc^{\bullet +}-BDP^{\bullet -}$ (1.60 eV) is comparable to that of the triplet BDP but substantially lower than the anticipated low-lying triplet Fc (see Fig. S3 in ESI[†] for energy diagram), one could expect the CR to the triplet states of Fc entity.¹²

Upon photoirradiation of the BDP entity of the triad 1 in deaerated PhCN, the characteristic absorption bands of the BDP^{•-} were observed at early time scale (~ 1 ps) (Fig. 4). At longer time scale, the band corresponding to BDP^{•-} at 590 nm decreased in intensity with concurrent build-up of the absorption band of $C_{60}^{\bullet-}$ at 1000 nm¹³ suggesting electronshift from the $BDP^{\bullet-}$ to the attached C_{60} entity forming $Fc^{\bullet +}-BDP-C_{60}^{\bullet -}$ as final CS state (see Fig. S4 in ESI[†] for decay curves). The rate constant of the charge-shift from BDP^{•-} to C₆₀ was determined to be 3.8×10^{11} s⁻¹. By following the decay of the $Fc^{\bullet +}-BDP-C_{60}^{\bullet -}$ in PhCN, the CR rate constant was determined to be 2.4×10^9 s⁻¹ from which a lifetime of 416 ps for the radical ion-pair was derived. The finding that the $\tau_{\rm RIP}$ of Fc⁺-BDP-C₆₀^{•-} is much longer than that of Fc^{•+}-BDP^{•-} ($k_{CR} = 5.8 \times 10^{10} \text{ s}^{-1}$; $\tau_{RIP} = 17 \text{ ps}$) reveals the effect of the electron shift mechanism in prolonging the τ_{RIP} in the triad 1. The photochemical events are summarised as in Fig. S5 (ESI[†]). Excitation of the central boron dipyrrin of the triad 1 results in abstraction of an



Fig. 4 Femtosecond spectra of Fc–BDP (left) and Fc–BDP–C₆₀ (right) in deaerated PhCN. $\lambda_{ex} = 460$ nm.



Fig. 5 Femtosecond (left) and nanosecond (right) transient absorption spectra of TPA–BDP in deaerated PhCN.

electron from the ferrocene entity to produce boron dipyrrin anion radical which subsequently undergoes electron shift to produce fullerene anion radical. As a result of relatively distant positioning of the cation and anion radicals charge stabilization is accomplished in the ferrocene–boron dipyrrin–fullerene triad in spite of closely disposed donor and acceptor entities.

The femtosecond measurements of the dyad, 2a by using 460 nm light in PhCN showed absorption bands at 590 and 690 nm corresponding to the boron dipyrrin radical anion and TPA radical cation, respectively (Fig. 5).¹¹ This observation suggests the electron transfer from the TPA to the attached BDP forming TPA^{•+}–BDP^{•–}. Interestingly, the k_{CR} of TPA^{•+}–BDP^{•–} was found to be $6.1 \times 10^8 \text{ s}^{-1}$, from which $\tau_{\rm RIP}$ was evaluated as 1.6 ns. The complementary nanosecond transient measurements with 510 nm laser excitation revealed absorption bands at 430 and 600 nm, in addition to the bleaching at 510 nm. These long-lived absorption bands are attributed to the triplet state of BDP. Because the formation of the triplet BDP is not efficient in the case of the reference 1b, the formation of triplet BDP may occur via CR of the radicalion-pair of 2a by taking into account the energy level of ³TPA*–BDP (1.58 eV) is lower than that of TPA $^{\bullet+}$ –BDP $^{\bullet-}$ (2.00 eV) (see Fig. S6 in ESI[†]).

Photoirradiation of the triad 2 in a deaerated PhCN solution revealed the characteristic absorption band of C_{60}^{\bullet} in the NIR region with a maximum at 1000 nm (see Fig. S7 in ESI†).^{2,13} The absorption band of TPA $^{\bullet +}$ was not observed, suggesting that the formation of the $C_{60}^{\bullet-}$ results from electron transfer from the singlet excited BDP, as electron donor, to the C₆₀. Such electron transfer is exothermic $(-\Delta G_{\rm CR} = 1.77 \text{ eV} \text{ and } -\Delta G_{\rm CS} = 0.45 \text{ eV})$. The $k_{\rm CR}$ value of the TPA-BDP^{•+}-C₆₀^{•-} was determined to be 2.0×10^9 s⁻¹, from which the τ_{RIP} was evaluated as 500 ps. The finding that the $\tau_{\rm RIP}$ of triad 2 is shorter than that of dyad 2a suggests the absence of the electron-shift and/or hole-migration processes between the TPA, BDP and C_{60} entities of 2, by taking into consideration the energy level of TPA-BDP \bullet^+ -C₆₀ \bullet^- (1.77 eV) is comparable to that of TPA^{•+}-BDP-C₆₀[•] (1.64 eV) (see Fig. S8 in ESI⁺). At longer time scale (1800 ps), the spectrum revealed the characteristic absorption of the triplet C₆₀ suggesting that the radical-ion pair decays through CR to populate the triplet C_{60} . This was also the conclusion based on nanosecond transient absorption measurements (see Fig. S9 in ESI[†]). The spectra in this time scale lacked bands of the radical ion-pairs instead an absorption band at 700 nm corresponding to the ${}^{3}C_{60}$ * was observed.¹⁴

In summary, charge stabilization in the donor–acceptor₁– acceptor₂ type molecular triad composed of closely spaced ferrocene–boron dipyrrin-fullerene, but not in triphenylamineboron dipyrrin–fullerene is reported. Excitation of the central boron dipyrrin of **1** results in abstraction of an electron from the ferrocene entity to produce boron dipyrrin anion radical which subsequently undergoes electron shift to produce fullerene anion radical. As a result of relatively distant positioning of the cation and anion radicals charge stabilization is accomplished in the ferrocene–boron dipyrrin–fullerene triad in spite of closely disposed donor and acceptor entities.

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