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Photoinduced Electron Transfer in a Ferrocene–Distyryl BODIPY Dyad and a Ferrocene–Distyryl BODIPY–C_{60} Triad**

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A ferrocene–distyryl BODIPY dyad and a ferrocene–distyryl BODIPY–C_{60} triad are synthesized and characterized. Upon photoexcitation at the distyryl BODIPY unit, these arrays undergo photoinduced electron transfer to form the corresponding charge-separated species. Based on their redox potentials, determined by cyclic voltammetry, the direction of the charge separation and the energies of these states are revealed. Femtosecond transient spectroscopic studies reveal that a fast charge separation ($k_{CS} = 1.0 \times 10^{10}$ s^{-1}) occurs for both the ferrocene–distyryl BODIPY dyad and the ferrocene–distyryl BODIPY–C_{60} triad, but that a relatively slow charge recombination is observed only for the triad. The lifetime of the charge-separated state is 500 ps. Charge recombination of the dyad and triad leads to population of the triplet excited sate of ferrocene and the ground state, respectively.

1. Introduction

Solar-light conversion is a promising strategy to address the increasing energy requirements in the future.[1] Intensive work has been carried out to develop highly efficient solar cells based on inorganic semiconductors with a narrow band gap.[2] As an alternative approach, artificial photosynthetic models have also received considerable attention, in which different chromophores and redox-active units are carefully selected and assembled to mimic the primary events of natural photosynthesis.[3–11] The ultimate goal is to convert solar energy into fuels effectively via a series of photochemical processes.

Being a versatile class of functional dyes, boron dipyrromethenes (BODIPYs) are promising candidates for the construction of such models as a result of their desirable photophysical and electrochemical properties.[12] In fact, a substantial number of BODIPY-based light-harvesting[13] and electron donor–acceptor[14] systems have been reported. By extending the π-conjugation via condensation with aryl aldehydes at the 3- and 5-positions, the resulting distyryl BODIPYs, labeled as DSBDPs, absorb and emit strongly in the near-infrared region (ca. 650 nm). In addition, they have reasonably long excited-state lifetimes and possess good solubility and stability in many solvent systems. As a result, apart from their application as fluorescent probes for metal ions,[15] components for molecular logic gates,[15c,16] and photosensitizers for photodynamic therapy,[17] these compounds have also been used to construct photosynthetic models[13c,g,18] and dye-sensitized solar cells.[19]

We have recently reported a dyad of DSBDP and C_{60}, which undergoes photoinduced electron transfer to give a charge-separated state with a lifetime of 476 ps in benzonitrile.[20] We report herein a related dyad and a related triad having DSBDP as an antenna, electron acceptor, and electron mediator, as well as ferrocene (Fc) and C_{60} as an electron donor and acceptor, respectively. The preparation and photoinduced electron-transfer properties of the Fc-DSBDP dyad and Fc-DSBDP-C_{60} triad are described in detail. The combination of DSBDP, Fc, and C_{60} enables the construction of excellent photosynthetic reaction center models that absorb over a wide range of visible light. The Fc-DSBDP-C_{60} triad is of particular interest as it undergoes sequential electron transfer resulting in charge stabilization.

2. Results and Discussion

Scheme 1 shows the synthetic route used to prepare these DSBDP-based arrays. Condensation of the phenol-containing BODIPY **1**[21] with one equivalent of aldehyde **2**[22] in the pres-

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[**] BODIPY: Boron Dipyrromethene

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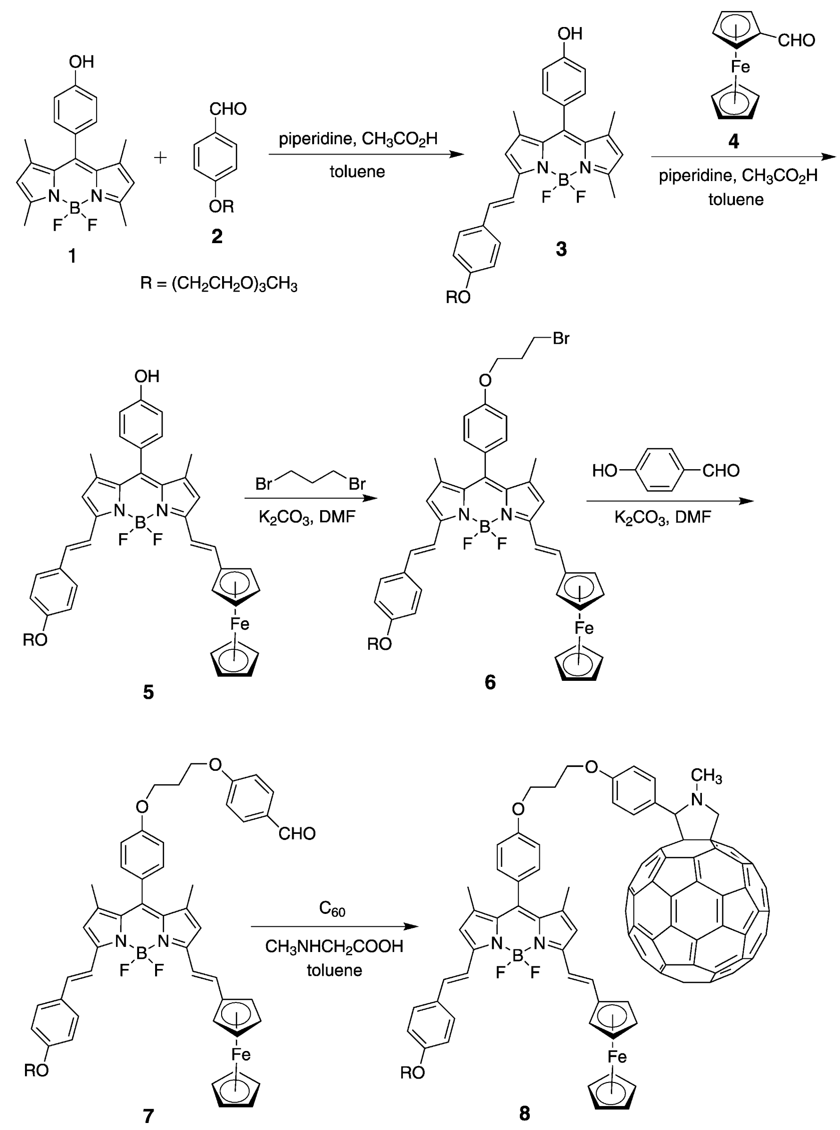
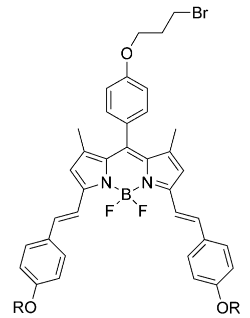


Scheme 1. Synthesis of the DSBDP-based arrays.

ence of piperidine and acetic acid gave the monostyryl BODIPY **3**, which could be isolated from the reaction mixture by column chromatography. Treatment of this compound with ferrocenecarboxaldehyde (**4**) under the same conditions led to the formation of Fc-DSBDP dyad **5**. This compound was then treated with 1,3-dibromopropane and 4-hydroxybenzaldehyde successively in the presence of K_2CO_3 in *N*,*N*-dimethylformamide (DMF) to afford aldehyde **7** via the bromo compound **6**. The Fc-DSBDP-C_{60} triad **8** was prepared by treating **7** with C_{60} and sarcosine according to the Prato procedure.[23] All the new compounds were characterized with various spectroscopic methods.



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R = $(CH_2CH_2O)_3CH_3$

Figure 1 a shows the absorption spectra of Fc-DSBDP dyad **6** and Fc-DSBDP-C_{60} triad **8** in benzonitrile. The spectrum of the non-Fc-containing analogue **9**[20] is also included for comparison. The spectrum of **9** exhibited a strong S_0–S_1 transition at 649 nm and a higher-energy S_0–S_2 transition at 376 nm. From the S_0–S_1 transition, the energy of the singlet-excited state of DSBDP (^{1}DSBDP*) was estimated as 1.91 eV. This transition was red-shifted by about 150 nm compared to that of the BODIPY derivatives as a result of the extended conjugation. The S_0–S_1 transition band of the unsymmetrical Fc-DSBDP dyad **6** was significantly broadened and red-shifted by about 20 nm compared to that of **9**, while the higher-energy S_0–S_2 transition was blue-shifted by about 15 nm. Under these conditions, the absorption of the Fc unit was not observed due to its low molar extinction coefficient. These observations suggested the presence of ground-state interactions between the Fc and DSBDP entities in the dyad. For Fc–DSBDP–C_{60} triad **8**, the absorption spectrum resembled that of dyad **6**, except for the occurrence of two additional characteristic absorption bands of C_{60} at 330 and 432 nm. The latter was partially overlapped with the S_0–S_2 absorption band of DSBDP.

Upon excitation at the DSBDP unit at 380 nm, DSBDP **9** gave a strong fluorescence band at 670 nm together with a weak one at 591 nm. The fluorescence quantum yield (Φ_f) was found to be 0.54. The presence of the Fc moiety in dyad **6** and triad **8** effectively quenched ^{1}DSBDP* ($\Phi_f = 1\times10^{-3}$), leading to virtually invisible fluorescence emission (Figure 1 b).

To establish the relative energy levels, electrochemical studies were performed for these compounds in benzonitrile using cyclic voltammetry. Figure 2 shows the voltammograms of DSBDP **9**, dyad **6**, and triad **8**. The voltammogram of DSBDP **9** showed an one-electron reduction couple at −1050 mV and an one-electron oxidation couple at 800 mV, both relative to the saturated calomel electrode (SCE). For the dyad **6**, the first reduction potential shifted cathodically to −996 mV (vs. SCE). An additional couple due to the one-electron oxidation of the Fc unit also appeared at 504 mV (vs. SCE), which is shifted to the

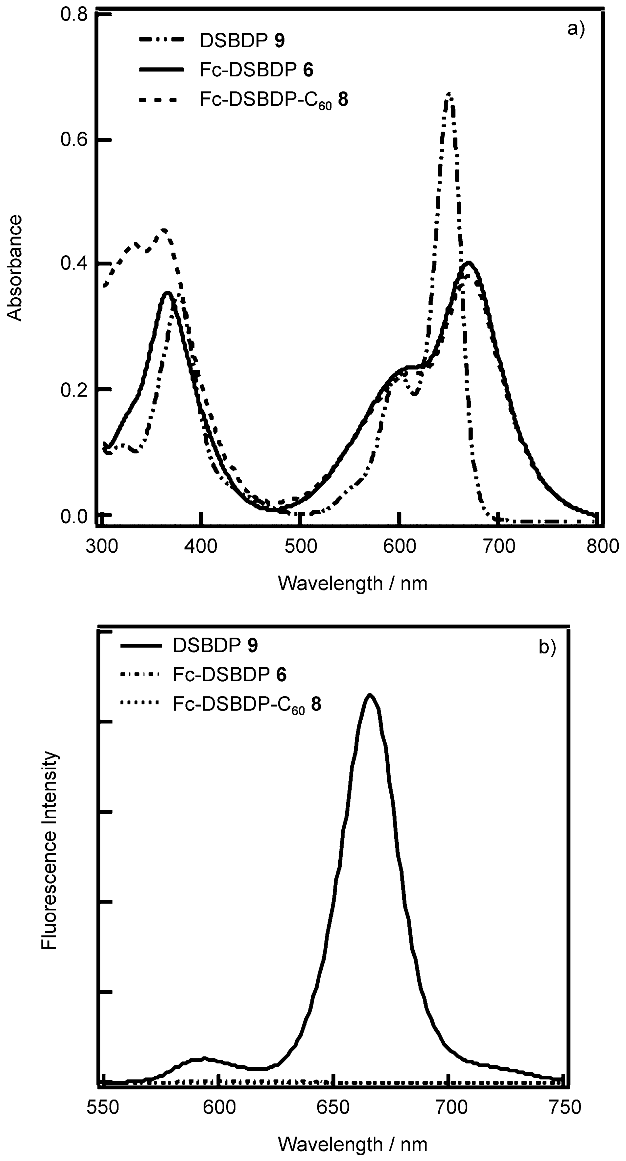

Figure 1. a) Electronic absorption and b) fluorescence spectra of DSBDP **9**, Fc-DSBDP dyad **6**, and Fc-DSBDP-C_{60} triad **8** in benzonitrile (all at 9 μм) ($\lambda_{ex}=380$ nm).

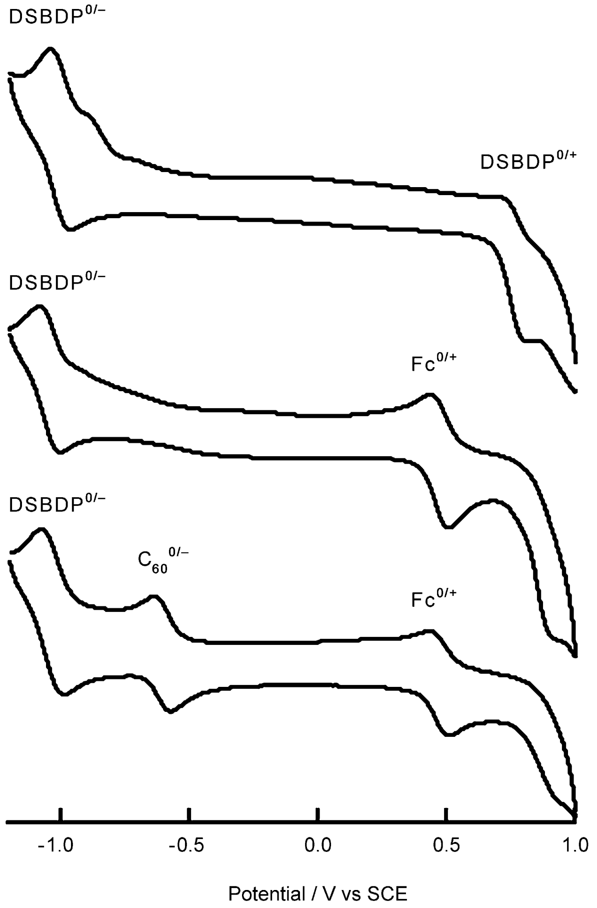

Figure 2. Cyclic voltammograms of DSBDP **9**, Fc-DSBDP dyad **6**, and Fc-DSBDP-C_{60} triad **8** (from top to bottom) in deaerated benzonitrile in the presence of 0.1 м [$n\text{Bu}_4\text{N}$][ClO_4]. Scan rate = 20 mV s^{-1}.

positive potential by about 30 mV as compared with that of ferrocene.[24] For the triad **8**, the position of the Fc/Fc^+ couple was virtually the same as that for the dyad **6**. Two reduction processes were also revealed at −996 and −576 mV (vs. SCE), which can be ascribed to the DSBDP and C_{60} moieties, respectively. Hence, the first reduction potential of the C_{60} unit is cathodically shifted by 420 mV as compared with that of the DSBDP unit.

These results clearly revealed the electron-donating nature of the Fc unit and the electron-accepting property of the DSBDP and C_{60} moieties in the dyad and triad. The energies of the charge-separated states were calculated by the Rehm–Weller equation[25] using the above spectroscopic and redox data. Based on the redox potentials of the first oxidation of Fc and the first reduction of DSBDP and C_{60} moieties, the driving forces of the charge-recombination process (ΔG_{CR}) for Fc^+-DSBDP$^{\cdot-}$ and Fc^+-DSBDP-$C_{60}^{\cdot-}$ were estimated to be −1.50 and −1.08 eV, respectively.[26] By comparing the energy level of these charge-separated states with that of ^{1}DSBDP* (1.91 eV), the driving forces of the charge-separation process (ΔG_{CS}) for Fc^+-DSBDP$^{\cdot-}$ and Fc^+-DSBDP-$C_{60}^{\cdot-}$ were determined to be −0.41 and −0.83 eV, respectively.[26] The negative values of ΔG_{CS} for these processes suggested that the generation of charge-separated state via ^{1}DSBDP* is thermodynamically favorable for these arrays in polar benzonitrile.

The excited-state properties of dyad **6** and triad **8** in benzonitrile were studied by femtosecond transient absorption spectroscopy using an excitation light source of 390 nm to selectively excite the DSBDP unit. As a reference, DSBDP **9** was first studied and the spectrum is shown in Figure 3. It can be seen that two absorption bands at 480 and 965 nm appear, which can be attributed to ^{1}DSBDP*. By monitoring the decay of the near-infrared band at 965 nm, it was found that it decayed slowly with a rate constant of 7.1×10^8 s^{-1} to populate the corresponding triplet manifold. The transient absorption spectra of the Fc-DSBDP dyad **6** (Figure 4) also showed the characteristic absorptions of ^{1}DSBDP*. However, the absorption at 844 nm decayed much faster with a rate constant of 9.8×10^9 s^{-1}, showing that ^{1}DSBDP* in the dyad is much short-lived

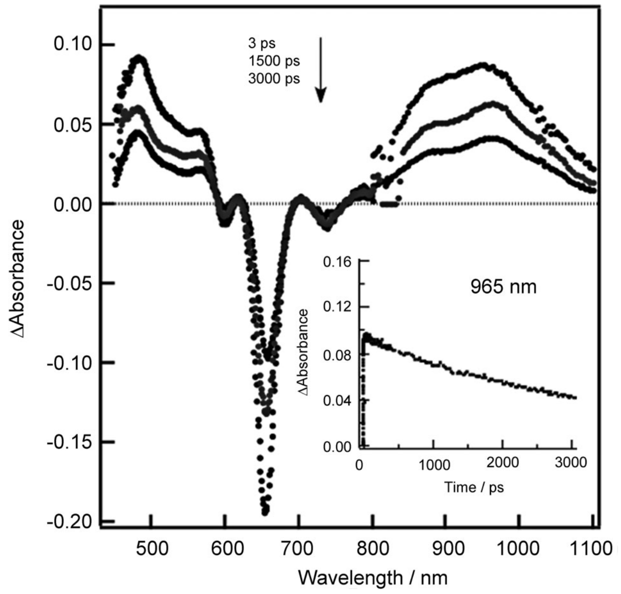

Figure 3. Femtosecond transient absorption spectral traces at different time intervals for DSBDP **9** in benzonitrile ($\lambda_{ex}=390$ nm). Inset: Decay profile of the transient band of ^{1}DSBDP* at 965 nm.

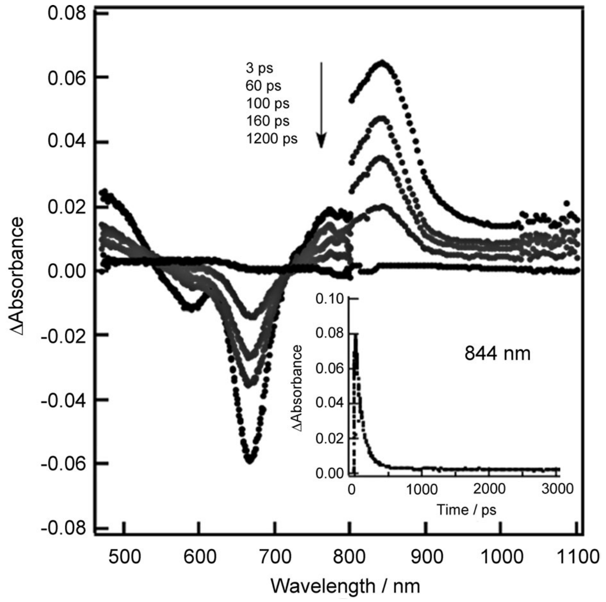

Figure 4. Femtosecond transient absorption spectral traces at different time intervals for Fc-DSBDP dyad **6** in benzonitrile ($\lambda_{ex}=390$ nm). Inset: Decay profile of the transient band of ^{1}DSBDP* at 844 nm.

than that in **9**. This observation is in accord with the occurrence of electron transfer from Fc to ^{1}DSBDP* in the dyad, as suggested by the effective fluorescence quenching and the negative calculated value of ΔG_{CS}. The short distance between the iron center of Fc and the boron center of DSBDP (6.2 Å as found in the optimized structure shown in Figure S1 in the Supporting Information) may rationalize the extremely fast electron-transfer process from Fc to ^{1}DSBDP*. The expected absorption band of DSBDP$^{\cdot-}$ was embedded by the strong bleaching of ^{1}DSBDP*. The transient absorption band of Fc$^+$ was also not observed due to its low molar extinction coefficient ($\varepsilon=330\,\text{M}^{-1}\text{cm}^{-1}$ at 620 nm).[27] For these reasons, we could not determine accurately the rate of charge recombination of Fc$^+$-DSBDP$^{\cdot-}$.

The complementary nanosecond transient absorption spectra of Fc-DSBDP dyad **6** in deaerated benzonitrile were also recorded by utilizing a laser source of 600 nm, which excited the DSBDP entity. The spectra (Figure S2 in the Supporting Information) showed no transient absorptions for the triplet excited state of DSBDP (^{3}DSBDP*) and Fc (^{3}Fc*) in the microsecond region. Energetically, the decay of Fc$^+$-DSBDP$^{\cdot-}$ to populate the ^{3}DSBDP* (1.15 eV)[20] and/or ^{3}Fc* (1.16 eV)[28] is possible. However, as ^{3}DSBDP* was not detected, it is likely that Fc$^+$-DSBDP$^{\cdot-}$ decays mainly to populate ^{3}Fc*, which is extremely difficult to detect in the microsecond region, as well as to the ground state.

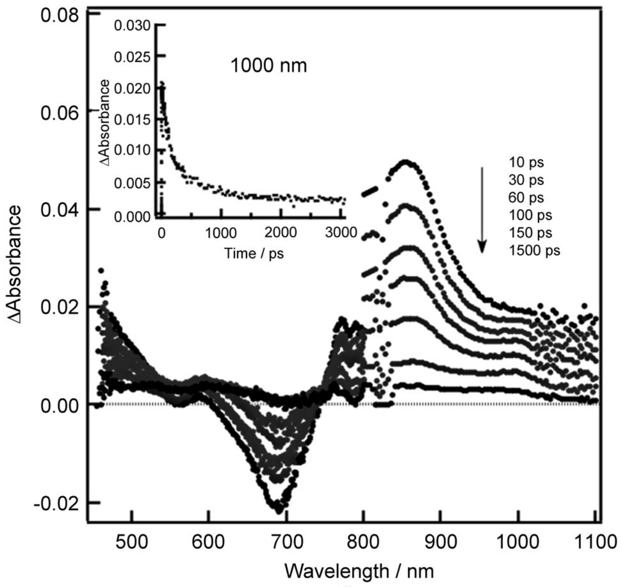

Figure 5. Femtosecond transient absorption spectral traces at different time intervals for Fc-DSBDP-C$_{60}$ triad **8** in benzonitrile ($\lambda_{ex}=390$ nm). Inset: Decay profile of the transient band of C$_{60}^{\cdot-}$ at 1000 nm.

For Fc-DSBDP-C$_{60}$ triad **8**, the transient absorption spectrum at 10 ps showed the characteristic absorption of ^{1}DSBDP* at 840 nm, which decayed rapidly with a rate constant of $1.0\times10^{10}\,\text{s}^{-1}$. For the transient spectra at time intervals between 30–1500 ps, the characteristic absorption of C$_{60}^{\cdot-}$ at 1000 nm could also be seen (Figure 5). These observations suggest the occurrence of electron transfer from Fc to ^{1}DSBDP* to form the initial charge-separated species Fc$^+$-DSBDP$^{\cdot-}$-C$_{60}$, which is followed by a fast electron mediation (EM) from DSBDP$^{\cdot-}$ to the C$_{60}$ to generate the final charge-separated species Fc$^+$-DSBDP-C$_{60}^{\cdot-}$. The transient band of C$_{60}^{\cdot-}$ at 1000 nm showed a fast decay within the initial 500 ps, followed by a slow decay up to 3 ns (inset of Figure 5). While the fast decay is quite similar to the decay of ^{1}DSBDP*, the slow decay can be assigned to the decay of Fc$^+$-DSBDP-C$_{60}^{\cdot-}$. From the fitting of the slow decay, the rate of charge-recombination (k_{CR}) and lifetime (τ_{CS}) of the

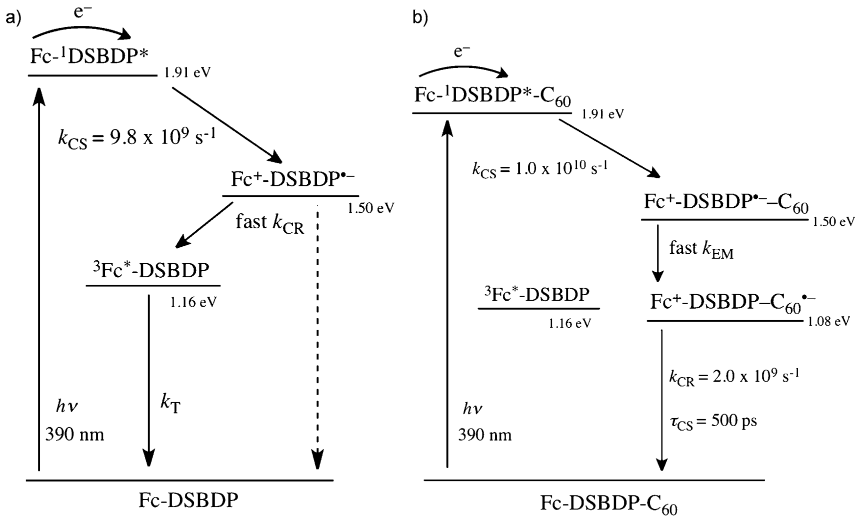

Figure 6. Energy-level diagrams showing the photoinduced intramolecular events of a) Fc-DSBDP dyad **6** and b) Fc-DSBDP-C_{60} triad **8** in benzonitrile.

charge-separated state Fc^{+}-DSBDP-$\mathrm{C}_{60}^{\cdot-}$ were found to be $2.0\times 10^{9}\,\mathrm{s}^{-1}$ and 500 ps, respectively. The latter is comparable with that of the closely spaced Fc^{+}-BODIPY-$\mathrm{C}_{60}^{\cdot-}$ triad (416 ps)[14b] and the $\mathrm{DSBDP}^{\cdot+}$-$\mathrm{C}_{60}^{\cdot-}$ dyad (476 ps)[20] reported by us earlier. Charge recombination resulted in population of the ground state. The photoinduced intramolecular processes of dyad **6** and triad **8** in benzonitrile are summarized in the energy-level diagrams shown in Figure 6.

3. Conclusions

We have reported the preparation and photoinduced electron-transfer processes of an Fc-DSBDP dyad and an Fc-DSBDP-C_{60} triad in benzonitrile. Upon excitation at the DSBDP unit, both of these systems undergo rapid electron transfer to form the charge-separated species Fc^{+}-$\mathrm{DSBDP}^{\cdot-}$, Fc^{+}-$\mathrm{DSBDP}^{\cdot-}$-C_{60}, and Fc^{+}-DSBDP-$\mathrm{C}_{60}^{\cdot-}$. Steady-state emission and femtosecond laser flash photolysis studies have provided tangible evidence for the occurrence of photoinduced electron transfer in these donor-acceptor systems. Free-energy calculations have also revealed that these charge-separation processes are thermodynamically favorable. The Fc-DSBDP-C_{60} triad **8** undergoes a fast charge separation ($1.0\times 10^{10}\,\mathrm{s}^{-1}$) and a relatively slow charge recombination ($2.0\times 10^{9}\,\mathrm{s}^{-1}$). The wide absorption of this triad in the visible region and its high k_{CS}/k_{CR} ratio suggest that this novel triad is a promising light-harvesting system.

Experimental Section

Materials

All the reactions were performed under nitrogen atmosphere. Tetrahydrofuran (THF), toluene, and DMF were distilled from sodium benzophenone ketyl, sodium, and barium oxide, respectively. Benzonitrile used for spectroscopic studies was of analytical grade (Aldrich). All other solvents and reagents were of reagent grade and used as received. Chromatographic purifications were performed on silica gel (Macherey–Nagel, 70–230 mesh) columns with the indicated eluents. Compounds **1**,[21] **2**,[22] and **9**[20] were prepared as described.

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker AVANCE II 400 spectrometer (^{1}H, 400; ^{13}C, 100.6 MHz) in $\mathrm{CDCl_3}$. Spectra were referenced internally using the residual solvent (^{1}H: $\delta = 7.26$ ppm) or solvent (^{13}C: $\delta = 77.0$ ppm) resonance relative to $\mathrm{SiMe_4}$. Electrospray ionization (ESI) mass spectra were measured on a Thermo Finnigan MAT 95 XL mass spectrometer. Steady-state fluorescence spectra were measured on a Shimadzu RF-5300 PC spectrofluorometer equipped with a photomultiplier tube having high sensitivity in the 700–800 nm region. The fluorescence quantum yields were measured with a Hamamatsu C9920-0X(PMA-12) U6039-05 spectrofluorometer with an integrated sphere adapted to a right angle configuration. The diffuse reflectance spectra of the samples were recorded and the measured results were corrected for the detector response as a function of wavelength.

Cyclic voltammograms were recorded on a BAS CV-50W voltammetric analyzer. A platinum disk electrode was used as the working electrode, while a platinum wire served as a counter electrode. The SCE electrode was used as the reference electrode. All measurements were carried out in deaerated benzonitrile containing 0.1 M [$n\mathrm{Bu_4N}$][$\mathrm{ClO_4}$] as the supporting electrolyte. The scan rate was set as 20 mV s^{-1}.

For laser flash photolysis, the studied compounds were excited by a Panther OPO pumped by an Nd:YAG laser (Continuum SLII-10, 4–6 ns fwhm) with a power of 1.5 or 3.0 mJ pulse^{-1}. The transient absorption measurements were performed using a continuous xenon lamp (150 W) as the probe light and an InGaAs-PIN photodiode (Hamamatsu 2949) as the detector. The output from the photodiode and a photomultiplier tube was recorded with a digitizing oscilloscope (Tektronix TDS3032, 300 MHz). Femtosecond transient absorption spectroscopic experiments were conducted 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 was derived from the fundamental output of Integra-C (780 nm, 2 mJ pulse^{-1}, 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 to 1660 nm, while the rest of the output was used for white light generation. Typically, 2500 excitation pulses were averaged for 5 s 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 using fresh solutions in each laser excitation.

Monostyryl BODIPY 3

A mixture of the phenol-containing BODIPY **1** (0.34 g, 1.0 mmol), aldehyde **2** (0.27 g, 1.0 mmol), glacial acetic acid (2.0 mL, 34.9 mmol), piperidine (2.4 mL, 24.3 mmol), and a small amount of $Mg(ClO_4)_2$ in toluene (60 mL) was refluxed for 3 h. The water formed during the reaction was removed azeotropically with a Dean–Stark apparatus. The mixture was concentrated under reduced pressure, then the residue was purified by column chromatography using CH_2Cl_2/ethyl acetate (10:1 v/v) as the eluent. The pink colored fraction was collected and rotary evaporated to yield the desired product (0.15 g, 26%). ^{1}H NMR: $\delta = 7.52$ (d, $J = 16.4$ Hz, 1H, CH=CH), 7.49 (d, $J = 8.8$ Hz, 2H, ArH), 7.15 (d, $J = 16.4$ Hz, 1H, CH=CH), 7.07 (d, $J = 8.8$ Hz, 2H, ArH), 6.94 (d, $J = 8.8$ Hz, 2H, ArH), 6.88 (d, $J = 8.8$ Hz, 2H, ArH), 6.55 (s, 1H, pyrrole-H), 6.34 (br s, 1H, OH), 5.98 (s, 1H, pyrrole-H), 4.15 (t, $J = 4.8$ Hz, 2H, CH_2), 3.87 (t, $J = 4.8$ Hz, 2H, CH_2), 3.73–3.78 (m, 2H, CH_2), 3.64–3.72 (m, 4H, CH_2), 3.54–3.59 (m, 2H, CH_2), 3.39 (s, 3H, OCH_3), 2.58 (s, 3H, CH_3), 1.47 (s, 3H, CH_3), 1.45 ppm (s, 3H, CH_3); ^{13}C{^{1}H} NMR: $\delta = 159.5$, 156.7, 154.3, 153.2, 142.7, 142.2, 140.2, 135.9, 133.2, 132.0, 129.6, 129.5, 128.9, 126.8, 120.9, 117.4, 117.0, 116.0, 114.9, 71.8, 70.8, 70.6, 70.5, 69.7, 67.4, 59.0, 14.8, 14.7, 14.5 ppm; MS (ESI): isotopic clusters peaking at *m/z* 613 {100%, $[M+Na]^+$}, 590 {17%, $[M]^+$}, and 571 {52%, $[M-F]^+$}; HRMS (ESI): *m/z* calcd for $C_{33}H_{37}BF_2N_2NaO_5$ $[M+Na]^+$: 613.2656, found 613.2659.

Fc-DSBDP Dyad 5

According to the above procedure, the monostyryl BODIPY **3** (0.59 g, 1.0 mmol) was treated with ferrocenecarboxaldehyde (**4**) (0.42 g, 2.0 mmol), glacial acetic acid (2.0 mL, 34.9 mmol), piperidine (2.4 mL, 24.3 mmol), and a small amount of $Mg(ClO_4)_2$ in refluxing toluene (60 mL) for 24 h. The crude product was purified by column chromatography using CH_2Cl_2/ethyl acetate (2:1 v/v) as the eluent. The blue-colored fraction was collected and rotary evaporated to yield the desired product (0.25 g, 32%). ^{1}H NMR: $\delta = 7.58$ (d, $J = 16.0$ Hz, 1H, CH=CH), 7.55 (d, $J = 8.8$ Hz, 2H, ArH), 7.32 (d, $J = 16.0$ Hz, 1H, CH=CH), 7.19 (d, $J = 16.0$ Hz, 1H, CH=CH), 7.15 (d, $J = 8.8$ Hz, 2H, ArH), 7.10 (d, $J = 16.0$ Hz, 1H, CH=CH), 6.95 (d, $J = 8.4$ Hz, 2H, ArH), 6.93 (d, $J = 8.4$ Hz, 2H, ArH), 6.59 (s, 1H, pyrrole-H), 6.56 (s, 1H, pyrrole-H), 5.36 (s, 1H, OH), 4.64 (t, $J = 1.8$ Hz, 2H, Fc-H), 4.43 (t, $J = 1.8$ Hz, 2H, Fc-H), 4.14–4.20 (m, 7H, CH_2 + Fc-H), 3.89 (t, $J = 4.8$ Hz, 2H, CH_2), 3.74–3.79 (m, 2H, CH_2), 3.65–3.73 (m, 4H, CH_2), 3.54–3.59 (m, 2H, CH_2), 3.39 (s, 3H, OCH_3), 1.50 (s, 3H, CH_3), 1.47 ppm (s, 3H, CH_3); ^{13}C{^{1}H} NMR: $\delta = 159.3$, 156.6, 152.9, 151.7, 142.0, 141.1, 137.7, 136.9, 135.0, 133.6, 133.4, 129.9, 129.7, 128.9, 127.0, 117.3, 116.8, 115.9, 114.8, 82.0, 71.9, 70.8, 70.6, 70.5, 70.4, 69.7, 68.1, 67.4, 59.0, 14.8 ppm; MS (ESI): an isotopic cluster peaking at *m/z* 786 {100%, $[M]^+$}; HRMS (ESI): *m/z* calcd for $C_{44}H_{45}BF_2$ FeN_2O_5 $[M]^+$: 786.2734, found 786.2729.

Fc-DSBDP Dyad 6

Potassium carbonate (0.55 g, 4.0 mmol) was added to a mixture of **5** (0.15 g, 0.2 mmol) and 1,3-dibromopropane (0.81 g, 4.0 mmol) in DMF (15 mL). The resulting mixture was stirred at room temperature overnight. The volatiles were then evaporated under reduced pressure and the residue was mixed with CH_2Cl_2 (40 mL) and water (40 mL). The aqueous layer was separated and extracted with CH_2Cl_2 (40 mL x 3). The combined organic fractions were dried over anhydrous $MgSO_4$, then evaporated to dryness. The residue was purified by column chromatography using CH_2Cl_2 as the eluent to give **6** as a blue solid (0.17 g, 94%). ^{1}H NMR: $\delta = 7.59$ (d, $J = 16.0$ Hz, 1H, CH=CH), 7.56 (d, $J = 8.4$ Hz, 2H, ArH), 7.32 (d, $J = 16.0$ Hz, 1H, CH=CH), 7.21 (d, $J = 8.4$ Hz, 2H, ArH), 7.20 (d, $J = 16.0$ Hz, 1H, CH=CH), 7.10 (d, $J = 16.0$ Hz, 1H, CH=CH), 7.02 (d, $J = 8.4$ Hz, 2H, ArH), 6.94 (d, $J = 8.4$ Hz, 2H, ArH), 6.60 (s, 1H, pyrrole-H), 6.57 (s, 1H, pyrrole-H), 4.64 (t, $J = 1.6$ Hz, 2H, Fc-H), 4.44 (t, $J = 1.6$ Hz, 2H, Fc-H), 4.13–4.21 (m, 9H, Fc-H + CH_2), 3.89 (t, $J = 4.8$ Hz, 2H, CH_2), 3.74–3.79 (m, 2H, CH_2), 3.61–3.73 (m, 6H, CH_2), 3.55–3.59 (m, 2H, CH_2), 3.39 (s, 3H, OCH_3), 2.38 (quintet, $J = 6.0$ Hz, 2H, CH_2), 1.50 (s, 3H, CH_3), 1.47 ppm (s, 3H, CH_3); ^{13}C{^{1}H} NMR: $\delta = 159.4$, 159.1, 152.9, 151.9, 142.0, 141.0, 137.5, 136.9, 134.9, 133.5, 133.2, 129.7, 129.6, 128.8, 127.6, 117.3, 116.8, 114.9, 114.8, 81.9, 71.8, 70.8, 70.6, 70.5, 69.7, 69.6, 68.1, 67.4, 65.4, 59.0, 32.3, 29.9, 29.6, 14.8 ppm; MS (ESI): isotopic clusters peaking at *m/z* 929 {100%, $[M+Na]^+$}, 908 {75%, $[M]^+$}, and 889 {35%, $[M-F]^+$}; HRMS (ESI): *m/z* calcd for $C_{47}H_{50}BBrF_2FeN_2NaO_5$ $[M+Na]^+$: 929.2206, found 929.2183.

Fc-DSBDP Dyad 7

Potassium carbonate (0.16 g, 1.2 mmol) was added to a mixture of **6** (0.18 g, 0.2 mmol) and 4-hydroxybenzaldehyde (0.07 g, 0.6 mmol) in DMF (30 mL). The resulting mixture was stirred at 80 °C for 8 h, then the solvent was removed under reduced pressure. The residue was then mixed with CH_2Cl_2 (50 mL) and water (50 mL). The aqueous layer was separated and extracted with CH_2Cl_2 (50 mL × 3). The combined organic fractions was dried over anhydrous $MgSO_4$, then evaporated to dryness. The residue was subject to column chromatography using CH_2Cl_2 as the eluent to give **7** as a blue solid (0.17 g, 89%). ^{1}H NMR: $\delta = 9.90$ (s, 1H, CHO), 7.85 (d, $J = 8.8$ Hz, 2H, ArH), 7.58 (d, $J = 16.0$ Hz, 1H, CH=CH), 7.56 (d, $J = 8.8$ Hz, 2H, ArH), 7.32 (d, $J = 16.0$ Hz, 1H, CH=CH), 7.21 (d, $J = 8.8$ Hz, 2H, ArH), 7.19 (d, $J = 16.0$ Hz, 1H, CH=CH), 7.10 (d, $J = 16.0$ Hz, 1H, CH=CH), 7.05 (d, $J = 8.8$ Hz, 2H, ArH), 7.02 (d, $J = 8.8$ Hz, 2H, ArH), 6.94 (d, $J = 8.8$ Hz, 2H, ArH), 6.59 (s, 1H, pyrrole-H), 6.56 (s, 1H, pyrrole-H), 4.64 (t, $J = 1.6$ Hz, 2H, Fc-H), 4.44 (t, $J = 1.6$ Hz, 2H, Fc-H), 4.31 (t, $J = 6.0$ Hz, 2H, CH_2), 4.23 (t, $J = 6.0$ Hz, 2H, CH_2), 4.15–4.20 (m, 7H, Fc-H + CH_2), 3.89 (t, $J = 4.8$ Hz, 2H, CH_2), 3.73–3.78 (m, 2H, CH_2), 3.65–3.72 (m, 4H, CH_2), 3.55–3.59 (m, 2H, CH_2), 3.39 (s, 3H, OCH_3), 2.34 (quintet, $J = 6.0$ Hz, 2H, CH_2), 1.48 (s, 3H, CH_3), 1.46 ppm (s, 3H, CH_3); ^{13}C{^{1}H} NMR: $\delta = 190.7$, 163.8, 159.4, 159.2, 153.0, 151.6, 141.9, 140.9, 137.5, 137.0, 135.0, 133.5, 133.3, 132.0, 130.0, 129.8, 129.7, 128.8, 127.6, 117.4, 117.2, 116.8, 114.9, 114.8, 114.7, 81.9, 71.9, 70.8, 70.6, 70.5, 69.7, 68.1, 67.4, 64.8, 64.2, 59.0, 29.1, 14.8 ppm; MS (ESI): isotopic clusters peaking at *m/z* 971 {52%, $[M+Na]^+$} and 948 {100%, $[M]^+$}; HRMS (ESI): *m/z* calcd for $C_{54}H_{55}BF_2FeN_2O_7$ $[M]^+$: 948.3414, found 948.3411.

Fc-DSBDP-C_{60} Triad 8

Dyad **7** (47 mg, 0.05 mmol) and sarcosine (44 mg, 0.50 mmol) were added to a solution of C_{60} (72 mg, 0.10 mmol) in toluene (50 mL). The mixture was heated under reflux for 12 h. After cooling slowly to room temperature, the solvent was removed under reduced pressure. The residue was purified by column chromatography using toluene, and then toluene/ethyl acetate (10:1 v/v) as the eluents. The product was obtained as a dark purple solid (43 mg, 51%). ^{1}H NMR: $\delta = 7.73$ (br s, 2H, ArH), 7.58 (d, $J = 16.0$ Hz, 1H, CH=CH), 7.56 (d, $J = 8.8$ Hz, 2H, ArH), 7.31 (d, $J = 16.0$ Hz, 1H, CH=CH), 7.19 (d, $J = 16.0$ Hz, 1H, CH=CH), 7.18 (d, $J = 8.8$ Hz, 2H, ArH), 7.09 (d, $J = 16.0$ Hz, 1H, CH=CH), 6.97–7.03 (m, 4H, ArH), 6.94 (d, $J = 8.8$ Hz, 2H, ArH), 6.58 (s, 1H, pyrrole-H), 6.55 (s, 1H, pyrrole-H), 4.98 (d, $J = 9.2$ Hz, 1H, pyrrolidine-H), 4.89 (s, 1H, pyrrolidine-H), 4.63 (t, $J = 1.8$ Hz, 2H, Fc-H), 4.44 (t, $J = 1.8$ Hz, 2H, Fc-H), 4.16–4.27 (m, 12H, Fc-H, pyrrolidine-H, and CH_2), 3.89 (t, $J = 4.8$ Hz, 2H, CH_2), 3.74–3.78 (m, 2H, CH_2), 3.66–3.72 (m, 4H, CH_2), 3.55–3.58 (m, 2H,

CH_2), 3.39 (s, 3H, OCH_3), 2.79 (s, 3H, NCH_3), 2.32 (quintet, $J = 6.4$ Hz, 2H, CH_2), 1.47 (s, 3H, CH_3), 1.45 ppm (s, 3H, CH_3); MS (ESI): an isotopic cluster peaking at m/z 1697 {100%, $[M+H]^+$}; HRMS (ESI): m/z calcd for $C_{116}H_{61}BF_2FeN_3O_6$ $[M+H]^+$: 1697.3999, found 1697.3951.

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[26] The driving forces of charge recombination (ΔG_{CR}) and charge separation (ΔG_{CS}) were calculated by the following equations: $\Delta G_{CR} = -e(E_{ox} - E_{red}) - \Delta G_s$ and $\Delta G_{CS} = -\Delta E_{0\text{-}0} - (\Delta G_{CR})$, where E_{ox} is the first oxidation potential of Fc, E_{red} is the first reduction potential of DSBDP or C_{60}, $\Delta E_{0\text{-}0}$ is the energy of the 0–0 transition energy gap between the lowest excited state and the ground state of DSBDP (1.91 eV), and ΔG_s refers to the static Coulombic energy in benzonitrile, which was neglected in the calculations.

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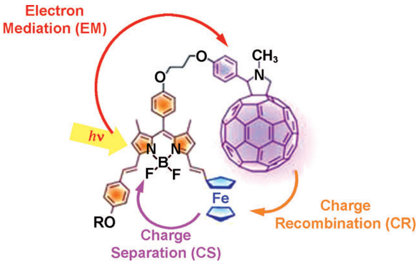
Photoinduced Electron Transfer in a Ferrocene–Distyryl BODIPY Dyad and a Ferrocene–Distyryl BODIPY–C_{60} Triad



Promising dyes: The photoinduced electron-transfer properties of a ferrocene–distyryl BODIPY dyad and a ferrocene–distyryl BODIPY–C_{60} triad (BODIPY: boron dipyrromethene) are studied. The triad undergoes a relatively slow charge recombination, giving a charge-separated state with a lifetime of 500 ps.