Long-Lived Charge Separation with High Quantum Yield in a Ferrocene-Porphyrin-Fullerene Triad

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A ferrocene-porphyrin-C_{60} triad was prepared to mimic efficient photosynthetic multistep electron transfer system. Upon irradiation, the triad produced a long-lived charge-separated state with a high quantum yield, compared with the previously reported artificial photosynthetic triads. The lifetime of the charge separated state increased with increasing the solvent polarity. These results indicate that C_{60} is an excellent building block as an acceptor in light energy conversion systems.

A number of donor-acceptor linked molecules have been prepared to understand the controlling factors of photosynthetic electron transfer (ET). Some of them such as triads, tetrads, and pentads, have displayed a long lifetime with a high quantum yield for the final charge-separated state, showing that photoinduced multistep ET is an effective strategy for the construction of artificial photosynthetic systems.[1,2] Recently fullerenes have been frequently employed as photosynthetic acceptors, because of their novel properties in ET.[3,4] We have shown that fullerenes accelerate charge separation (CS) and slow down charge recombination (CR) in donor-linked fullerene dyads due to the small reorganization energies (λ), which make it possible to optimize artificial photosynthetic multistep CS.[5,6] Thus, it is an additional promising strategy that fullerenes with small λ are used in multistep ET systems such as triads. Gust[7] and our group[8] reported the photodynamics of carotenoid (Car)-free base porphyrin (H_2P)-C_{60} and zincporphyrin (ZnP)-imide-C_{60} triads, respectively. However, the overall quantum yields (0.17-0.46) and the lifetimes (1.3-170 ns) of the charge-separated state are not so satisfactory, compared with those of conventional triads, tetrads, and pentads.[1,2] Here we report novel CR behavior of ferrocene (Fc) - ZnP - C_{60} triad **1** (Figure 1).[9] The energy gradients of each state in **1** are designed to be in the order of Fc-^{1}ZnP*-C_{60} > Fc-ZnP$^{\bullet+}$-$C_{60}^{\bullet-}$ > Fc$^{\bullet+}$-ZnP-$C_{60}^{\bullet-}$. Therefore, it will display a sequential ET within the molecule, as observed in the similar Car-H_2P-C_{60} triad;[7] Fc-^{1}ZnP*-C_{60} → Fc-ZnP$^{\bullet+}$-$C_{60}^{\bullet-}$ → Fc$^{\bullet+}$-ZnP-$C_{60}^{\bullet-}$.

The absorption spectrum of **1** in THF is essentially a linear combination of the absorption spectra of **4**, **5**, and **6**, indicating no evidence for strong interaction among the three chromophores in the ground state. Fluorescence spectra of **1** and **2** in THF are quenched strongly as compared with that of **4** when excited at the Soret band under the same concentration (relative intensities: 0.05 and 0.05). In contrast, the relative fluorescence intensity of the **3** vs. **4** (0.37) is much larger, suggesting that quenching of ^{1}ZnP* by the attached C_{60} is a dominant deactivation pathway in **1**. Nanosecond time-resolved transient absorption spectra of **1** were taken in benzonitrile. The typical examples are shown in Figure 2. Immediately after excitation of **1** with 532 nm nanosecond pulse, where the Fc, ZnP, and C_{60} were excited in a molar ratio of 2:79:19, the characteristic bands due to the C_{60} anion radical ($C_{60}^{\bullet-}$) appeared at around 700-1100 nm. In contrast, no

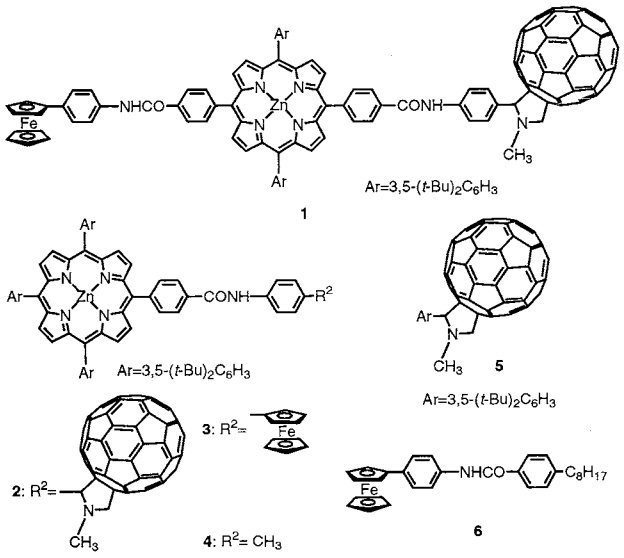

Figure 1. Structures of compounds **1-6**.

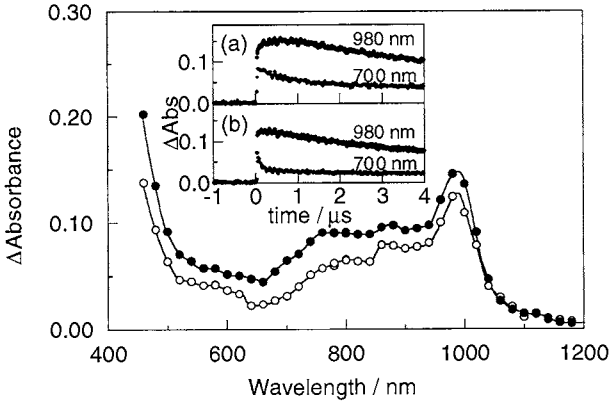

Figure 2. Transient absorption spectra of Fc-ZnP-C_{60} triad (0.1 mM) in deaerated benzonitrile at 250 ns (filled cricle) and 2.5 μs (open circle) after 532 nm-laser irradiation (16mJ/pulse). Insert: Time profiles; (a) in deaerated and (b) in O_2 saturated benzonitrile.

apparent absorption due to the zincporphyrin cation radical (ZnP$^{\bullet+}$) was observed. In our previous studies on a similar ZnP-C_{60} dyad,[5,6] the rate constants of CS (k_{CS1}) from ^{1}ZnP* to C_{60} are 0.9-1.2 × 10^{10} s^{-1} with quantum yields of 0.94-0.98 in polar solvents such as THF and DMF, whereas the CR rate (k_{CR1}) changes from 2 × 10^9 s^{-1} in THF to >5 × 10^{10} s^{-1} in DMF. Based on the results, we can conclude that initial photoinduced ET from ^{1}ZnP* to C_{60} occurs in **1**, followed by the charge-shift

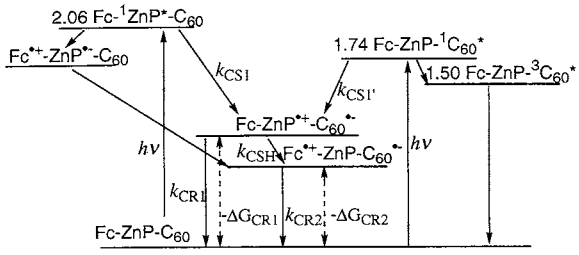

Figure 3. Schematic energy diagram for photoinduced reactions of Fc-ZnP-C_{60}. Characters indicate the energy revels relative to the ground state.

Table 1. Lifetimes of charge-separated states of the triad in various solvents

solvent [a]	ε_{solv}	$-\Delta G_{CR1}$ [b]	$-\Delta G_{CR2}$ [b]	k_{CR2} / s^{-1}	τ_{CR2} / μs
DMF	36.7	0.99	0.77	6.4×10^4	15.6
BN	25.2	1.01	0.80	1.3×10^5	7.5
ANS/BN	14.8	1.08	0.89	1.8×10^5	5.6
THF	7.58	1.22	1.10	2.7×10^5	3.7
ANS	4.33	1.44	1.41	3.6×10^5	2.8
ANS/Bz	3.31	1.60	1.64	4.0×10^6	0.25
Bz	2.28	1.90	2.07	2.4×10^7	0.04

[a]BN; benzonitrile, ANS; anisole, Bz; benzene, ANS/Bz =1:1 in vol, and ANS/BN =1:1 in vol. [b]in eV.

(CSH) from the Fc to $ZnP^{•+}$ to produce Fc$^{•+}$-ZnP-$C_{60}^{•-}$, as shown in Figure 3.[10,11]

The lifetime (τ_{CR2}) of Fc$^{•+}$-ZnP-$C_{60}^{•-}$ was obtained from the time-profile of absorbance at 980 nm under the O_2-saturated conditions to eliminate the significant contribution of ^{3}ZnP* and/or $^3C_{60}$* (Figure 1). The overall quantum yield for the photoinduced CS based on total light absorbed by both the porphyrin and C_{60} ($[C_{60}^{•-}] / ([^1ZnP^*] + [^1C_{60}^*])$) equals 0.65 in benzonitrile. Considering that the CSH is beyond the time resolution (10 ns) of our instrumentation, the rate constant of the charge-shift (k_{CSH}) is estimated to be 10^9-10^{11} s^{-1}. The value of τ_{CR2} in benzonitrile is 7.5 μs. It is highly remarkable that both the quantum yield and the lifetime in **1** are much improved, compared with those of conventional triads[1,2,12] as well as those of the similar Car-H_2P-C_{60} triad (τ_{CR2} = 170 ns, Φ = 0.14 in 2-methyltetrahydrofuran).[7]

The values of τ_{CR2}, k_{CR2}, $-\Delta G_{CR1}$, and $-\Delta G_{CR2}$ of **1** in various solvents are summarized in Table 1.[13] As the solvent polarity increases, the τ_{CR2} values increase up to 15.6 μs! Osuka et al. reported the photodynamics of zincporphyrin (ZnP) - pyromellitimide (Im) dyad and zincdiporphyrin (ZnDP) - ZnP - Im tetrads.[14] The long lifetime of ZnDP$^{•+}$-ZnP-Im$^{•-}$ (0.39-23 μs) was realized in polar solvents such as DMF, but the overall quantum yield (0.05-0.17 in THF) is poor. The lifetime of $ZnP^{•+}$-$Im^{•-}$ decreases with an increase of solvent polarity, whereas that of ZnDP$^{•+}$-ZnP-Im$^{•-}$ increases with an increase of solvent polarity. They proposed that in the latter case, superexchange interaction of the intervening ZnP π-orbital tends to facilitate the CR process. The solvent dependence of the CR process in **1** may be explained by the similar superexchange mechanism.

In conclusion, we have demonstrated that the present triad shows the highest balanced values for the quantum yield and the lifetime of the final charge-separated state, among the previously reported artificial photosynthetic triads. These characteristics are quite favorable for the triad to apply to solar energy conversion systems. Detailed studies on the photodynamics together with those of the corresponding dyads are in progress.

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9 The synthesis of **1** will be reported elsewhere in details.
10 It was quite difficult to detect the ferrocene cation radical because of the small extinction coefficient.
11 Based on the energy level diagram of **1** in polar solvents such as THF and benzonitrile, photoinduced CS from ZnP to $^1C_{60}$* may occur to generate the Fc-ZnP$^{•+}$-$C_{60}^{•-}$.
12 A. Osuka, S. Marumo, N. Mataga, S. Taniguchi, T. Okada, I. Yamazaki, Y. Nishimura, T. Ohno, and K. Nozaki, *J. Am. Chem. Soc.*, **118**, 155 (1996).
13 $-\Delta G_{CR} = E_{ox} - E_{red} + \Delta Gs$, $-\Delta G_{CS} = \Delta E_{0\text{-}0} - (-\Delta G_{CR})$, $\Delta Gs = e^2/(4\pi\varepsilon_0)[(1/(2R^+) + 1/(2R^-) - 1/R_{cc})(1/\varepsilon_S) - (1/(2R^+) + 1/(2R^-))(1/\varepsilon_r)]$ where $\Delta E_{0\text{-}0}$ is energy of the 0-0 transition between the S_1 and S_0 states for the porphyrin, E_{ox} and E_{red} are the first oxidation potential of the donor and the first reduction potential of the acceptor in CH_2Cl_2, respectively, R^+ and R^- are radii of D and A, respectively, R_{cc} is center-to-center distance between the two moieties, and ε_S and ε_r are static dielectric constants of solvent used and when measured the redox potentials, respectively: R^+= 5.0 Å for the porphyrin, R^+= 3.7 Å for the Fc, R^-= 4.4 Å for the C_{60}, R_{cc}=18.0 Å between P and C_{60}, R_{cc}=34.2 Å between Fc and C_{60}. Although the Born equation does not give correct values for ΔG_S in nonpolar solvents such as anisole and benzene because of overestimation of the polarity, the values of $-\Delta G_{CR}$ were estimated tentatively.
14 A. Osuka, S. Nakajima, K. Maruyama, N. Mataga, T. Asahi, I. Yamazaki, Y. Nishimura, T. Ohno, and K. Nozaki, *J. Am. Chem. Soc.*, **115**, 4577 (1993).