Intramolecular Electron Transfer

Production of an Ultra-Long-Lived Charge-Separated State in a Zinc Chlorin–C_{60} Dyad by One-Step Photoinduced Electron Transfer**

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The natural photosynthetic reaction center utilizes sequential multistep electron transfer from the excited chromophore to the terminal electron acceptor via electron mediators, which are well-organized in a protein matrix, to attain a long lifetime (as long as seconds) of the final charge-separated (CS) state.[1] A number of linked electron-donor–acceptor dyads have been developed to mimic such multistep electron-transfer processes in natural photosynthesis. These systems have been extended to triads and more complex systems in which electron mediators are combined to achieve a longer lifetime of the final CS state.[2–7] A long lifetime of 380 ms, which is comparable to the lifetime of the natural system, has been achieved using a well-designed molecular tetrad (namely, ferrocene-zinc porphyrin-free base porphyrin-fullerene).[8] However, a significant amount of energy is lost during the multistep electron-transfer processes in both the natural and model systems. Thus, it is highly desired to develop donor–acceptor dyad systems in which the CS state has long lifetimes and does not lose energy by sequential electron transfer. The lifetime of the CS state has recently been reported to be elongated by decreasing the distance between the donor and acceptor in the dyads.[9–11]

We report herein that a zinc chlorin–fullerene dyad which has an extremely short donor–acceptor distance (ZnCh–C_{60}, Figure 1)[12–14] has a CS state with the longest lifetime reported for a linked donor–acceptor system. The large temperature dependence of the lifetime of the CS state has been examined over a wide temperature range (−150 to 65 °C).

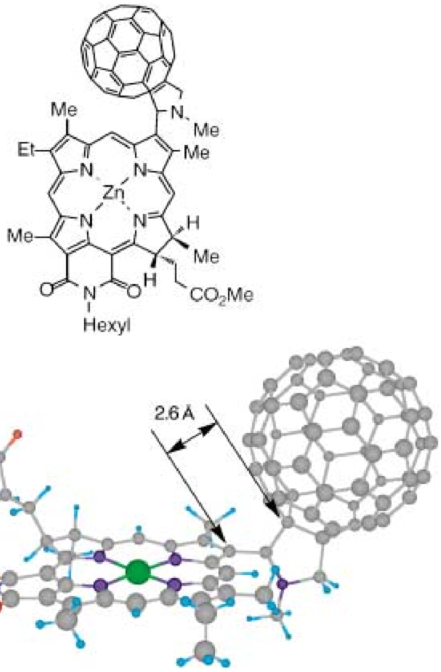

Figure 1. Structure of the ZnCh–C_{60} dyad, as well as the optimized structure determined by PM3 calculations.

The ZnCh–C_{60} dyad was synthesized by 1,3-dipolar cycloaddition of the 3-formylchlorin and sarcocine with fullerene.[13] The tetrapyrrolic compound contains a six-membered fused-imide ring system and presents an opportunity to design a fullerene conjugate containing a spacer with a defined

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Supporting information for this article (the cyclic voltammogram of the dyad in PhCN, picosecond transient absorption spectra of ZnCh–C_{60}, and analytical data) is available on the WWW under http://www.angewandte.org or from the author.

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length and geometry. The optimized structure of the dyad was obtained by PM3 calculations (Figure 1), and the edge-to-edge distance was determined to be 2.6 Å.

The absorption spectrum of ZnCh–C_{60} in benzonitrile (PhCN) is a reasonable superposition of the spectra of the component chromophores making up the dyads. Thus, there is no significant electronic interaction between the individual chromophores in the ground-state configuration despite the short linkage. The cyclic voltammogram of ZnCh–C_{60} in deaerated PhCN containing 0.1 M Bu_4NClO_4 consists of three one-electron reductions of the C_{60} molecule in the dyad (−0.53, −1.09, and −1.60 V versus the standard calomel electrode (SCE)), two one-electron reductions of ZnCh (−0.94 and −1.46 V), and a single one-electron oxidation of ZnCh (0.73 V; see the Supporting Information).

Photoexcitation of a deoxygenated solution of ZnCh–C_{60} in PhCN with 410-nm monochromatized light results in fluorescence with an emission maximum at 730 nm. The fluorescence decay was monitored at 730 nm, which corresponds to the emission of the zinc chlorin moiety.[9] The lifetime of the zinc chlorin fluorescence ($\tau = 2.7$ ns in an unlinked state)[9] was significantly reduced when it was in the dyad (τ(ZnCh–C_{60}) = 10 ps) as a result of electron transfer from the singlet excited state of ZnCh (^{1}ZnCh*) to the C_{60} molecule of the dyad. The rate constant of electron transfer (k_{ET}) from ^{1}ZnCh* to C_{60} was determined as $1.0 \times 10^{11}\,s^{-1}$ from the difference between the reciprocal lifetimes of ZnCh–C_{60} and the unlinked zinc chlorin. The change in the free energy of the photoinduced electron transfer (ΔG^0_{ET}) from the ^{1}ZnCh* moiety to the C_{60} moiety in PhCN was determined as −0.44 eV from the one-electron oxidation potential and the excitation energy ($S_1 = 1.70$ eV) of the ZnCh moiety, as well as the one-electron reduction potential of the C_{60} moiety in ZnCh–C_{60}.

The k_{ET} value was also determined by picosecond transient absorption measurements. Application of a 388-nm laser pulse to a deoxygenated solution of ZnCh–C_{60} in PhCN gave rise to a transient absorption maximum at 460 nm, which corresponds to the singlet excited state of ZnCh (S2). The decay rate constant was determined as $1.0 \times 10^{11}\,s^{-1}$, which agrees with the value determined from measurements of the fluorescence lifetime. The decay of the absorbance at 460 nm, which corresponds to ^{1}ZnCh*, is accompanied by an increase in an absorbance at 590 nm, which results from the formation of ZnCh$^{\bullet+}$ (S2). This observation indicates that electron transfer from ^{1}ZnCh* to C_{60} occurs to form the CS state ZnCh$^{\bullet+}$–$C_{60}^{\bullet-}$.

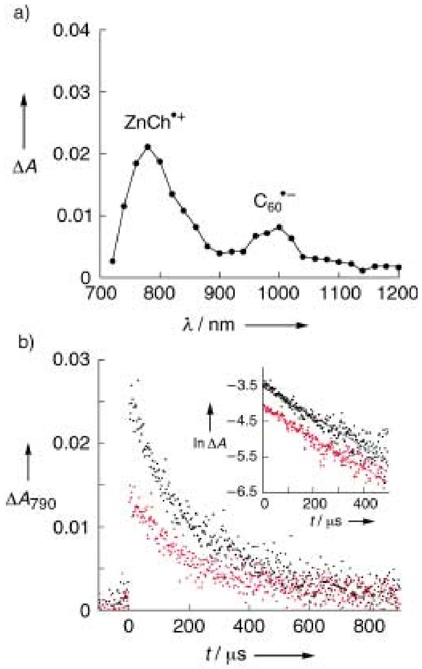

Figure 2. a) Transient absorption spectrum of ZnCh–C_{60} (1.0×10^{-4} M) in deaerated PhCN at 25 °C taken 1.0 μs after laser excitation at 355 nm; b) decay profiles at 790 nm with different laser power (30 mJ, black circles; 10 mJ, red circles). Inset: first-order plots.

The CS state can also be detected as a transient absorption spectrum upon excitation (355 nm) of a deoxygenated solution of ZnCh–C_{60} in PhCN with a nanosecond laser pulse (Figure 2 a). The absorption band at 1000 nm is an attribute of the monofullerene radical anion.[8–11] The absorption band at 790 nm (Figure 2 a) agrees with that of the π-radical cation of zinc chlorin. Thus, the transient absorption spectrum shown in Figure 2 a indicates formation of the CS state (ZnCh$^{\bullet+}$–$C_{60}^{\bullet-}$). The quantum yield of the CS state was determined as 12 %,[15,16] which is smaller than the efficiency of the fluorescence quenching (99.6 %).[17] This result indicates that the singlet excited state is quenched to form a short-lived exciplex,[14] a part of which is converted into a long-lived CS state (Figure 2 a). The CS state decays by back electron transfer (BET) to the ground state rather than to the triplet excited state since the CS state is lower in energy (1.26 eV) than both the triplet excited states of C_{60} (1.50 eV) and ZnCh (1.36–1.45 eV).[9] The rate of BET (k_{BET}) was determined from the disappearance of the absorption band at 790 nm, which is attributable to the ZnCh$^{\bullet+}$ species in the ZnCh$^{\bullet+}$–$C_{60}^{\bullet-}$ dyad. The decay of the absorption band at 790 nm was monitored using different laser power, and the decay was found to obey first-order kinetics with the same slope observed for all laser powers (Figure 2 b). This observation indicates clearly that the decay of the CS state is ascribed to intramolecular BET and not to intermolecular BET. The k_{BET} value is determined as $4.2 \times 10^3\,s^{-1}$, and thus the lifetime of the CS state is 230 μs at 25 °C.

The ESR spectra were measured by photoirradiation of ZnCh–C_{60} in frozen PhCN (Figure 3 a). The resulting spectrum of the photoirradiated ZnCh–C_{60} in PhCN at −150 °C is shown in the inset of Figure 3 a. The ESR spectrum consists of two characteristic signals, one of which is attributable to an organofullerene radical anion with a g value (2.0007) smaller than the free-spin value (2.0023), and the other to the zinc chlorin radical cation with a higher g value (2.0033).[9,10,18] The disappearance of the ESR signal intensity obeyed first-order kinetics (Figure 3 a) under the experimental conditions, where a low concentration of ZnCh–C_{60} (1.0×10^{-5} M) was employed to avoid intermolecular decay of the CS state. The temperature dependence of the decay rate constant (k_{BET}) was examined in frozen PhCN by observing the decay of the ESR

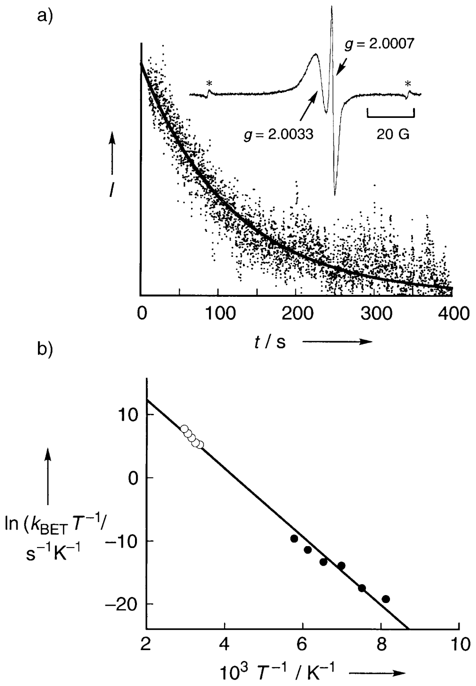

Figure 3. a) ESR spectrum and the decay time profile of the ESR signal intensity of $ZnCh^{\bullet+}$–$C_{60}^{\bullet-}$ in frozen PhCN at −150 °C. The asterisk denotes a Mn^{2+} marker; b) plot of $\ln(k_{BET}T^{-1})$ versus T^{-1} for BET in $ZnCh^{\bullet+}$–$C_{60}^{\bullet-}$ in PhCN as determined by laser flash photolysis (○) and ESR (●) measurements.

signal at −150 to −100 °C. The temperature dependence of the k_{BET} value in frozen PhCN (Figure 3b, filled circles) as well as in PhCN solution was observed by laser flash photolysis at 25–65 °C (Figure 3b, open circles). The activation enthalpy for the intramolecular BET was determined from the slope of the graph (Figure 3b) to be 5.4 kcal mol^{-1}. Such a large temperature dependence of the k_{BET} value indicates that the BET process is deeply in the Marcus inverted region because of the small amount of reorganization energy necessary for electron transfer in the ZnCh–C_{60} dyad with a short linkage and the rate of electron transfer decreases as the driving force increases.[19] This result is in sharp contrast with the case of the tetrad systems in which the BET is on the Marcus top region and the k_{BET} value exhibits no temperature dependence.[8,20] The lifetime of the CS state at −150 °C is as long as 120 s, which is the longest CS lifetime reported for linked donor–acceptor systems.

In summary, we have successfully shown that intramolecular electron transfer from the singlet excited state of zinc chlorin to fullerene occurs efficiently in a dyad with a short linkage. This process results in an ultra-long-lived CS state without the loss of energy that is inevitable in multistep electron-transfer processes.

Experimental Section

Ch–C_{60} dyad: A mixture of 3-formyl-3-devinylpurpurin-18-*N*-hexylimide methyl ester (104 mg, 1.0 equiv), C_{60} (127 mg, 1.1 equiv), and sarcosine (72 mg, 5.0 equiv) in dry toluene was refluxed under nitrogen for 17 h. The solution was cooled to room temperature and then passed through alumina (Brockmann Grade III) with dichloromethane as the eluent. The major fraction was collected, and the product obtained after evaporating the solvent was further purified by chromatography on alumina (Grade III) using hexanes/dichloromethane as the eluant (first 2/3 then 1/2 v/v) to give the title compound (67 mg) and recovered 3-formal-3-devinyl-purpurin-18-*N*-hexylimide methyl ester (25 mg). Analytical data are given in the Supporting Information.

ZnCh–C_{60}: A solution of zinc acetate dihydrate (500 mg) in methanol (15 mL) was added to a solution of the free-base dyad (42 mg) in chloroform (50 mL). The resultant solution was degassed by vacuum and stirred in a nitrogen atmosphere at room temperature for 19 h. The reaction mixture was then washed with water (6 × 50 mL), the organic layer collected, and then dried with sodium sulfate. After filtration, the solvent was removed and the title compound was obtained in quantitative yield. See the Supporting Information for analytical data.

The nanosecond and picosecond laser flash photolysis measurements were performed as reported previously.[9,21]

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[17] The decay of the absorbance at 590 nm (see Supporting Information), which is much faster than the decay shown in Figure 2b, may be ascribed to the decay of the exciplex. The residual absorbance at 3 ns in the data shown in the Supporting Information may correspond to the absorbance arising from $\mathrm{ZnCh}^{\bullet+}$ (Figure 2a), although the low signal-to-noise ratio has precluded the determination of the quantum yield from the picosecond laser measurements. It should be noted that the exciplex should have an absorption spectrum quite similar to the CS state.

[18] The observation of broad ESR signals arising from $\mathrm{ZnCh}^{\bullet+}$ and $C_{60}^{\bullet-}$ moieties indicate that the spin–spin interaction is not strong enough to produce the singlet or triplet state.

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