Photoinduced Electron Transfer

Fullerene-Terminated Dendritic Multiporphyrin Arrays: "Dendrimer Effects" on Photoinduced Charge Separation

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The development of light-harvesting antenna molecules for visible photons is one of the important subjects in the basic issue of solar-energy conversion in natural photosynthesis and also to their potential applications to molecular electronics.[1] Recently, we reported light-harvesting dendritic zinc porphyrin arrays which can efficiently capture visible photons and channel the excitation energy to the focal core.[2,3] This observation prompted us to integrate such dendritic dye molecules as light-harvesting antennas into electron-transfer relay systems. Here we report the molecular design and photoinduced electron-transfer properties of a series of fullerene-terminated dendritic zinc-porphyrin arrays nP_{Zn}-C_{60} (Scheme 1).[4] Covalently linked porphyrin–C_{60} dyads (P-C_{60}) have attracted a great deal of attention as novel photoinduced electron-transfer units,[5–7] in which the charge-separated (CS) state ($P^{\bullet+}$-$C_{60}^{\bullet-}$), which results from electron transfer from the porphyrin moiety to C_{60}, can take advantage of the low reorganization energy of C_{60}. Thus, the present study featuring C_{60}-terminated multiporphyrin arrays nP_{Zn}-C_{60} can make use of the well-established photochemistry of covalently linked porphyrin–C_{60} dyads. Herein, we highlight a unique effect of a large dendritic array ($7P_{Zn}$) on the lifetime of the CS state.

The arrays nP_{Zn}-C_{60} ($n = 1$, 3, and 7) were synthesized from hydroxy-terminated zinc-porphyrin dendrons (nP_{Zn}-OH) and a carboxylic acid appended C_{60} derivative (C_{60}-CO_2H), by using azodicarboxylic acid diethyl ester as a condensation agent, and unambiguously characterized by ^{1}H NMR and UV/Vis spectroscopies, as well as with MALDI-TOF-MS spectrometry.[8] For example, a solution of $7P_{Zn}$-C_{60} in benzonitrile (PhCN) showed an intense Soret absorption band at 417 nm arising from the zinc-porphyrin units and a weak C_{60} absorption band at 700 nm.[8] Comparison of this spectral profile with those of $7P_{Zn}$-OH and C_{60}-CO_2H as reference compounds showed only a slight broadening of the

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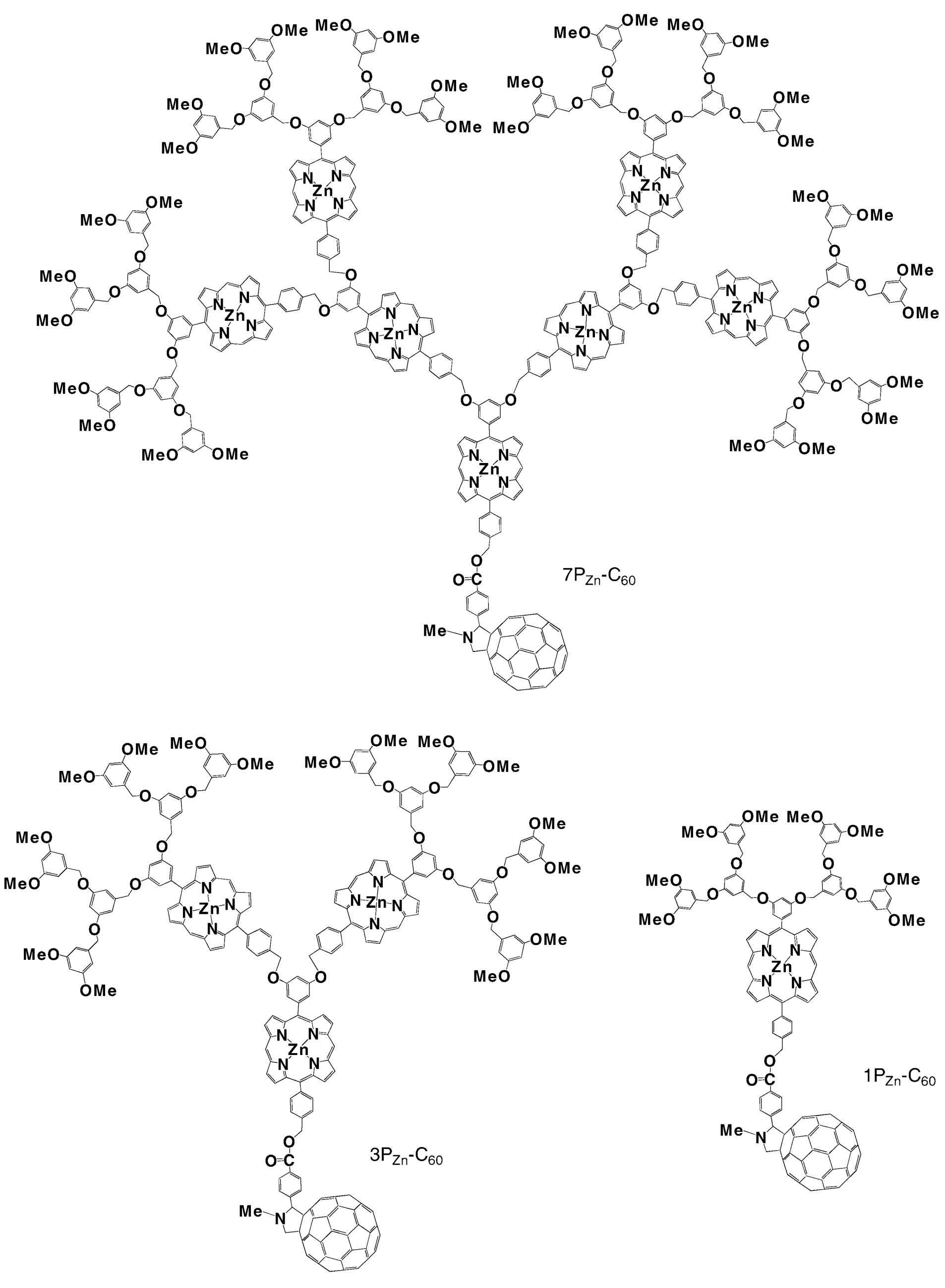

Scheme 1. Schematic structures of nP_{Zn}-C_{60}.

Soret absorption band (difference in the full-width at half-maximum (ΔFWHM) $= +54\,cm^{-1}$) without any shift, which indicates there is a negligibly weak ground-state interaction between the zinc-porphyrin units and the C_{60} terminus. Although $3P_{Zn}$-C_{60} and $1P_{Zn}$-C_{60} showed essentially the same characteristics in the absorption spectra as $7P_{Zn}$-C_{60}, the Soret absorption band became broader (FWHM increases from 572 to 947 cm^{-1}) as the generation number of the dendritic wedge increased, which suggests there is an electronic interaction among the P_{Zn} moieties in $7P_{Zn}$-C_{60}.

Excitation of a solution of $1P_{Zn}$-C_{60} in PhCN at 544 nm resulted in a zinc-porphyrin fluorescence with two major bands at 590 and 645 nm, while no fluorescence was detected from the C_{60} terminus.[8] The fluorescence of $1P_{Zn}$-C_{60} was clearly quenched by 84 ± 1 % relative to the reference system of $1P_{Zn}$-OH. As expected, the one-generation-higher $3P_{Zn}$-C_{60}, when $3P_{Zn}$-OH was used as the reference, showed a lower quenching efficiency (60 ± 2 %) than $1P_{Zn}$-C_{60}.[8] On the other hand, the quenching efficiency of $7P_{Zn}$-C_{60}, the largest homologue of the series, stayed at the same level as that of $3P_{Zn}$-C_{60} (62 ± 2 %; $7P_{Zn}$-OH as reference).[8] A similar trend was observed for the analysis by time-resolved spectroscopy. Excitation of solutions of nP_{Zn}-C_{60} ($n = 1$, 3, and 7) in PhCN under argon at 22 °C at 410 nm resulted in the fluorescence monitored at 610 nm (Figure 1a) having dual-exponential decay characteristics, where the relatively long-lived fluorescing components are assignable to residual components after the photochemical communication between the nP_{Zn} and C_{60} units.[8] The average rate constant for the fluorescence decay ($k_{CS} = [1/\tau_{FL}^{av}]_{sample} - [1/\tau_{FL}]_{ref}$) became smaller by a factor of

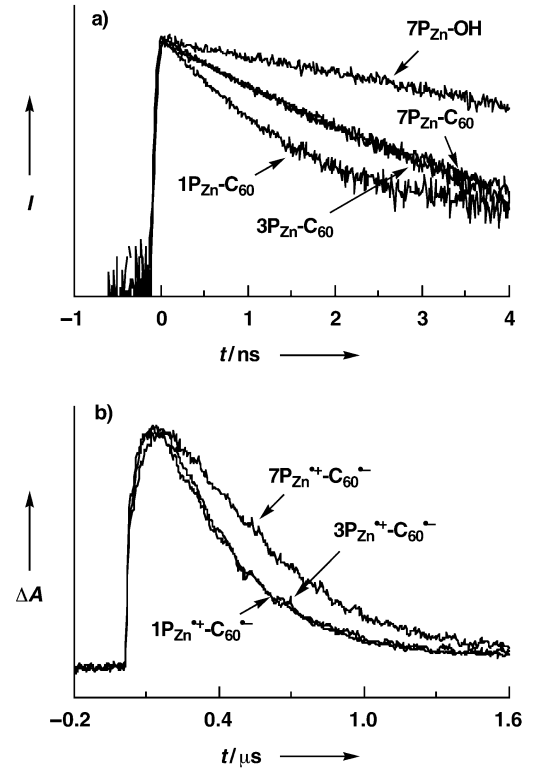

Figure 1. a) Fluorescence decay profiles of nP_{Zn}-C_{60} (n = 1, 3, and 7) at 610 nm upon excitation at 410 nm, and b) absorption decay profiles of $C_{60}^{\cdot-}$ at 1020 nm, generated upon excitation of nP_{Zn}-C_{60} (n = 1, 3, and 7) at 532 nm, in PhCN at 22 °C under argon.

four as the zinc-porphyrin array increased from $1P_{Zn}$-C_{60} ($1.55\times10^9\,s^{-1}$) to $3P_{Zn}$-C_{60} ($0.40\times10^9\,s^{-1}$; Figure 2, gray bars). On the other hand, the k_{CS} value ($0.43\times10^9\,s^{-1}$) of the largest homologue of the family ($7P_{Zn}$-C_{60}) was comparable to that of $3P_{Zn}$-C_{60}, in spite of the fact that $7P_{Zn}$-C_{60} has a greater number of the zinc-porphyrin units located away from the C_{60} terminus.

We found that the fluorescence quenching observed arises from a photoinduced electron-transfer reaction from the zinc-porphyrin units to the C_{60} terminus. Formation of an ion pair ($P_{Zn}^{\cdot+}$-$C_{60}^{\cdot-}$) was confirmed by means of picosecond time-resolved absorption spectroscopy. For example, excitation of a solution of $7P_{Zn}$-C_{60} in PhCN at 388 nm with a 150-fs laser pulse resulted in an absorption band at 450 nm corresponding to the singlet-excited state $^1P_{Zn}^*$, which decayed with a rate constant of $0.50\times10^9\,s^{-1}$.[8] This value is almost identical to the fluorescence decay rate constant (k_{CS}) observed for $7P_{Zn}$-C_{60} ($0.43\times10^9\,s^{-1}$) in PhCN. The transient absorption spectroscopy also showed a rise of the $P_{Zn}^{\cdot+}$ absorption at 650 nm, whose rate constant ($0.50\times10^9\,s^{-1}$) was again in agreement with the k_{CS} value of $7P_{Zn}$-C_{60}. The characteristic absorption band of the $C_{60}^{\cdot-}$ species appeared at 1020 nm.[8] These observations clearly indicate that the photoexcitation of the P_{Zn} units in $7P_{Zn}$-C_{60} is followed by an electron transfer from the resultant $^1P_{Zn}^*$ species to the C_{60} terminus to generate a charge-separated (CS) state ($P_{Zn}^{\cdot+}$-$C_{60}^{\cdot-}$). Hence, as shown in Figure 2, the rate constants for fluorescence decay (k_{CS}; gray bars) allowed evaluation of the quantum efficiencies of nP_{Zn}-C_{60} (n = 1, 3, and 7) for charge separation (Φ_{CS}, black bars).[8] Interestingly, the Φ_{CS} value of $7P_{Zn}$-C_{60} (51 %), which is smaller than that of $1P_{Zn}$-C_{60} (80 %), is comparable to the Φ_{CS} value of lower generation $3P_{Zn}$-C_{60} (49 %). This trend suggests that the large dendritic $7P_{Zn}$ array may serve as a better energy funnel than the lower generation $3P_{Zn}$, and allow the excitation energy to flow more efficiently into the focal core.

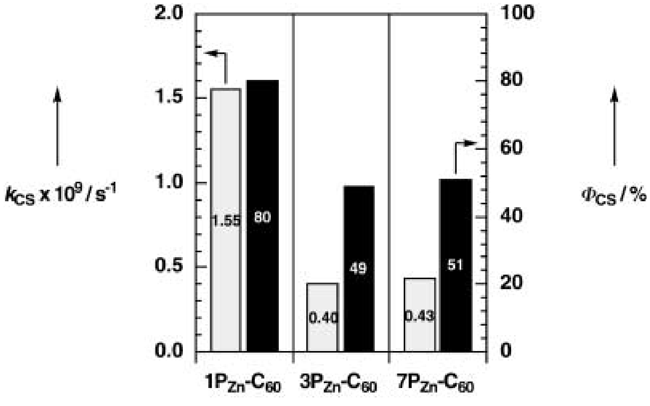

Figure 2. Fluorescence decay rate constants (k_{CS}) at 610 nm and quantum efficiencies of the charge separation (Φ_{CS}) of nP_{Zn}-C_{60} (n = 1, 3, and 7) upon excitation at 410 nm in PhCN at 22 °C under argon.

We investigated the charge recombination (CR) process by nanosecond time-resolved absorption spectroscopy of nP_{Zn}-C_{60} (n = 1, 3, and 7) at 600–1200 nm. Excitation of a solution of $7P_{Zn}$-C_{60} in PhCN at 532 nm with a 6-ns laser pulse gave an absorption band at 1020 nm, which correspond to $C_{60}^{\cdot-}$, and bands centered at 850 and 740 nm, which correspond to the triplet-excited $^3P_{Zn}^*$ and $^3C_{60}^*$ species,[9] respectively.[8] The time profile of the absorption corresponding to $C_{60}^{\cdot-}$ at 1020 nm (Figure 1 b) was analyzed for determination of the lifetime of the charge-separated state (τ_{CS}), and the decay curve nicely fitted with dual-exponential components. The slow-decaying component corresponded to the triplet-excited species, while a radical ion pair $P_{Zn}^{\cdot+}$-$C_{60}^{\cdot-}$ was identified as the fast-decaying component, whose τ_{CS} value was evaluated to be as long as 0.66 μs in PhCN at 22 °C. Very interestingly, $3P_{Zn}$-C_{60} and $1P_{Zn}$-C_{60} also showed similar transient absorption spectral characteristics in PhCN, but their τ_{CS} values (0.41 and 0.35 μs, respectively) were clearly shorter than that of $7P_{Zn}$-C_{60}. Accordingly, $7P_{Zn}$-C_{60} showed a smaller CR rate constant ($k_{CR} = (1.5\pm0.2)\times10^6\,s^{-1}$) than $1P_{Zn}$-C_{60} ($(2.9\pm0.3)\times10^6\,s^{-1}$) and $3P_{Zn}$-C_{60} ($(2.4\pm0.3)\times10^6\,s^{-1}$; Figure 3, gray bars).

We consider that the electron-transfer reaction in nP_{Zn}-C_{60} most likely takes place from the zinc-porphyrin unit directly connected to the C_{60} terminus, while the energy for the electron transfer is acquired by the dendritic antenna. We also propose another interesting role of the large dendritic antenna in the electron-transfer event. From the slowest back electron transfer process, observed for the largest dyad $7P_{Zn}$-C_{60}, we assume that the $P_{Zn}^{\cdot+}$ species, which is generated at the focal point of $7P_{Zn}$-C_{60} upon electron transfer, should move away from the $C_{60}^{\cdot-}$ terminus towards the periphery by an intramolecular hole hopping mechanism.[8] In relation to this proposal, the first oxidation potential (E^1_{ox}) of $7P_{Zn}$-C_{60} (0.29 V) was lower than those of $1P_{Zn}$-C_{60} (0.33 V) and $3P_{Zn}$-

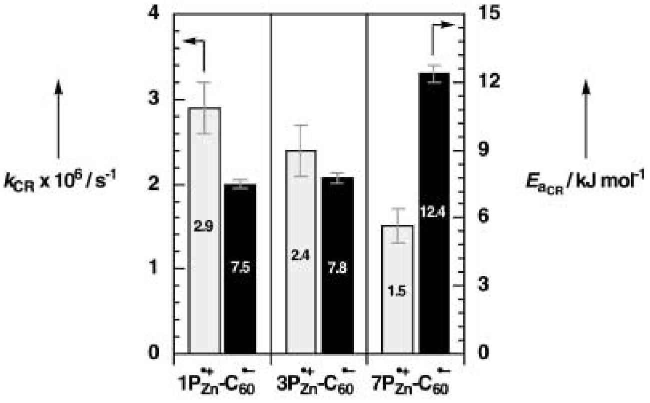

Figure 3. Charge recombination rate constants (k_{CR}, 22 °C) and activation energies (E_a^{CR}) for $nP_{Zn}^{\bullet+}$-$C_{60}^{\bullet-}$ ($n = 1$, 3, and 7) in PhCN under argon.

C_{60} (0.31 V).[10] As already suggested from the analysis of the band widths in the absorption spectra, this result may again indicate a large electronic interaction among the densely packed chromophores in $7P_{Zn}$-C_{60}. We also investigated the temperature dependencies of the k_{CR} values of nP_{Zn}-C_{60} ($n =$ 1, 3, and 7), which gave activation energies (E_a) for the charge recombination process (Figure 3, black bars). Quite interestingly, the E_a value for $7P_{Zn}$-C_{60} (12.4 kJ mol^{-1}) was much greater than those for the lower generation homologues (7.5 and 7.8 kJ mol^{-1} for $1P_{Zn}$-C_{60} and $3P_{Zn}$-C_{60}, respectively). This trend is consistent with the above proposal, since a thermally activated conformational motion of the dendritic chromophore array possibly allows folding of the large $7P_{Zn}^{\bullet+}$-$C_{60}^{\bullet-}$ dyad, thereby facilitating the collision of even topologically distant $P_{Zn}^{\bullet+}$ and $C_{60}^{\bullet-}$ species.

In conclusion, we have demonstrated with studies on the photoinduced electron transfer properties of the C_{60}-terminated dendritic zinc porphyrin arrays (nP_{Zn}-C_{60}; $n = 1$, 3, and 7) that the large dendritic antenna ($7P_{Zn}$) not only harvests visible light for the electron transfer to the C_{60} terminus, but also retards the back-electron-transfer process. These results indicate a new potential of dendronized dye molecules for the efficient conversion of solar energy into chemical potentials. Application of fullerene-terminated dendritic multiporphyrin arrays to solar cells is one of the subjects worthy of further investigation.

Experimental Section

$1P_{Zn}$-C_{60}, $3P_{Zn}$-C_{60}, and $7P_{Zn}$-C_{60} were prepared by coupling of the hydroxy-terminated zinc porphyrin dendrons $1P_{Zn}$-OH, $3P_{Zn}$-OH, and $7P_{Zn}$-OH with C_{60}-CO_2H, respectively.[8] Time-resolved fluorescence spectra were measured by a single-photon-counting method using a second harmonic generation (SHG, 410 nm) of a Ti:sapphire laser (Spectra-Physics, Tsunami 3950-L2S, FWHM = 1.5 ps) and a streakscope (Hamamatsu Photonics, C43334-01) equipped with a polychromator (Action Research, SpectraPro 150) as an excitation source and a detector, respectively. Picosecond transient absorption spectra were recorded by a pump and probe method, whereby samples were excited with a second harmonic generation (SHG, 388 nm) of an output from a femtosecond Ti:sapphire regenerative amplifier seeded by SHG of an Er-doped fiber (Clark-MXR CPA-2001 plus, 1 kHz, FWHM = 150 fs). The excitation light was depolarized, while the monitor white light was generated by focusing the fundamental of the laser light on a flowing D_2O/H_2O cell. The transmitted monitor light was detected with a dual MOS linear image sensor (Hamamatsu Photonics, C6140) or a InGaAs photodiode array (Hamamatsu Photonics, C5890-128). Nanosecond transient absorption spectroscopy was carried out using SHG (532 nm) of a Nd:YAG laser (Spectra-Physics, Quanta-Ray GCR-130, FWHM = 6 ns) as an excitation source. For obtaining transient absorption spectra in the near-IR region (600–1200 nm), the monitor light from a pulsed Xe lamp was detected with a Ge-APD (Hamamatsu Photonics, B2834). All the samples in a quartz cell (1 × 1 cm) were deaerated by bubbling the solutions with argon for 15 min. Cyclic voltammograms were obtained by using a conventional three-electrode system on a BAS CV-50W potentiostat/galvanostat. A platinum disk electrode was used as a working electrode, while a platinum wire served as a counter electrode. An Ag/AgCl electrode was used as a reference electrode. The potentials were referenced to an internal ferrocene/ferrocenium redox couple.

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[7] Gust and co-workers have reported the photochemical properties of a fullerene-appended star-shaped porphyrin pentamer (see refs. [6a] and [6e]).

[8] See Supporting Information.

[9] The decay of this absorption band was accelerated on introduction of O_2 as a triplet quencher.

[10] $[nP_{Zn}\text{-}C_{60}] = 0.1$ mM in PhCN containing 0.05 M Bu_4NClO_4 as a supporting electrolyte; scan rate = 0.1 V s^{-1}.