

Photoinduced charge separation and charge recombination of fullerene bearing dendritic poly(amidoamine) with carboxylates at the terminal in aqueous media†

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Photoinduced charge separation of fullerodendrimers with carboxylates at terminal sites ($C_{60}\sim COO^-$) has been found in aqueous media. Time-resolved transient absorption and fluorescence measurements of the fullerodendrimers demonstrated that charge separation takes place from the terminal carboxylate anion to the central excited singlet state of C_{60} , generating $C_{60}^{\cdot-}\sim COO^\cdot$ with high quantum efficiency in aqueous solution. In the presence of viologen dication and a sacrificial donor, the persistent viologen radical cation was generated.

Artificial photosynthetic reaction centres are based upon photoinduced electron transfer, whereby an excited state of a chromophore accepts or donates to a nearby electron donor or electron acceptor. If the resulting charge-separated state is energetic and long-lived, such a charge-separated state can be suitable for exploitation in additional energy-requiring processes. Recent reports of photoinduced electron transfer in various types of molecules consisting of a fullerene covalently linked to donors have demonstrated that fullerenes act as excellent electron acceptors for photoinduced electron transfer in various organic solvents.¹ Prominently, the fullerene sphere has been found to have small internal and solvent reorganization energies.² These features lead to desirable photoinduced electron transfer properties such as rapid charge separation and slow charge recombination in organic solvents.

Water-soluble fullerene derivatives³ have been investigated to date mostly within the framework of biological and medical applications. For example, C_{60} derivatives have been applied as HIV inhibitors,⁴ radical scavenging capabilities,⁵ and in anticancer studies.⁶ The reversible binding of a poly(amidoamine) substituted anthracene moiety to fullerene results in a water-soluble molecule which will be able to act as a biologically active agent releasing fullerene intracellularly.⁷ As for the photoinduced electron transfer of water-soluble fullerenes, a few reports dealing with intermolecular electron transfer events in the presence of water-soluble electron donors have been described,⁸ mono- and

multiply-carboxylated fullerene derivatives have been shown to perform intermolecular electron-capture reaction and intermolecular-electron transfer reaction in aqueous media.^{8a,b} Photoinduced electron transfer within Zn-cytochrome-c and a polyanionic fullerene dendrimer in the protein has been reported in aqueous media.^{8d}

From the viewpoint of photoinduced electron transfer in aqueous media, the photoactive fullerodendrimers are interesting. Our interest is to construct fullerodendrimers to induce charge separation within the dendrimers having the fullerene as an electron acceptor with an electron donor at terminal site in aqueous media under photoirradiation. Thus, in the present study, we employed water-soluble fullerodendrimers in which C_{60} is covalently linked with carboxylates at a terminal site *via* poly(amidoamine) dendrons, $C_{60}(Gn-COOK)$ (Chart 1). Herein, we reveal a unique charge-separation process of $C_{60}(Gn-COOK)$ by time-resolved fluorescence and transient absorption measurements.

Fullerodendrons $C_{60}(G1.5-COOMe)$, $C_{60}(G2.5-COOMe)$, $C_{60}(G1.5-COOK)$ and $C_{60}(G2.5-COOK)$ were prepared according to methods described previously.⁹ As shown in Fig. 1, the weak absorption bands of the C_{60} moiety appeared at 705 nm with strong absorption at shorter wavelengths than 400 nm.

Since the absorption of the dendron G2.5-COOK appears at shorter wavelength than 320–400 nm,¹⁰ the observed broadening of absorptions for $C_{60}(Gn-COOK)$ suggests the aggregation of $C_{60}(Gn-COOK)$ in aqueous solution. However, appearance of the absorption peak indicates that the aggregations are quite loose.

Excitation of $C_{60}(Gn-COOK)$ in H_2O with light at 600 nm resulted in characteristic C_{60} fluorescence with a band in the region of 680–850 nm with peaks at 720–740 nm (Fig. 2). Broadening of the fluorescence bands was also observed for $C_{60}(Gn-COOK)$ by comparison with $C_{60}(G1.5-COOMe)$ in

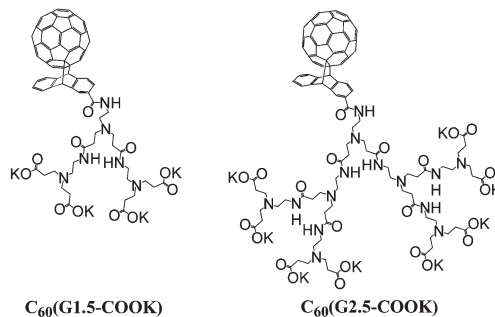


Chart 1

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† Electronic supplementary information (ESI) available: Experimental section, long time-profiles of $C_{60}(G1.5-COOK)$ and $C_{60}(G2.5-COOK)$ in the presence and absence of MV^{2+} and TEOA. See <http://dx.doi.org/10.1039/b508793g>

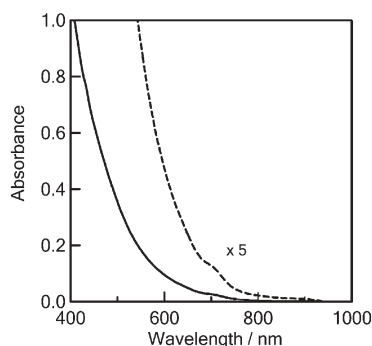


Fig. 1 Steady-state absorption spectra of $C_{60}(G2.5-COOK)$ (0.1 mM) in H_2O .

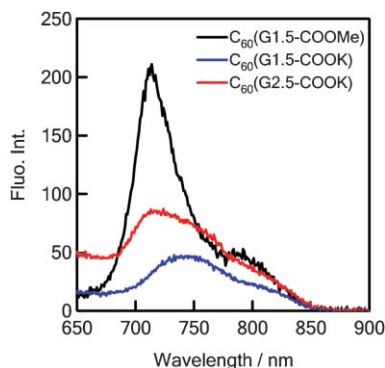


Fig. 2 Steady-state fluorescence spectra of $C_{60}(G1.5-COOK)$ and $C_{60}(G2.5-COOK)$ in H_2O and $C_{60}(G1.5-COOMe)$ in PhCN; concentration = 0.1 mM and $\lambda_{ex} = 600$ nm.

PhCN. Both $C_{60}(G1.5-COOK)$ and $C_{60}(G2.5-COOK)$ show a weak emission from the C_{60} moiety in H_2O compared with that from $C_{60}(G1.5-COOMe)$ in PhCN, indicating the efficient quenching of the excited singlet state of the C_{60} moiety; *i.e.*, the peak intensity decreased markedly by a factor of 75–80% in H_2O compared with that of the ester in PhCN. Furthermore, more efficient quenching of the fullerene emission in $C_{60}(G1.5-COOK)$ compared with $C_{60}(G2.5-COOK)$ was confirmed in Fig. 2.

In agreement to the steady-state fluorescence spectral behaviour, the picosecond fluorescence lifetime measurements revealed shortening of fluorescence lifetimes of fullerene moieties in both $C_{60}(G1.5-COOK)$ and $C_{60}(G2.5-COOK)$ in H_2O (Fig. 3). The emission decays of the fullerodendrimers were found to be almost a single exponential function, giving lifetimes ($\tau_{f,COOK}$) of 290 and 350 ps, respectively, for $C_{60}(G1.5-COOK)$ and $C_{60}(G2.5-COOK)$; these $\tau_{f,COOK}$ values were shorter than that of $C_{60}(Gn-COOMe)$ in PhCN ($\tau_{f,COOMe} = 1.4$ ns). The rates of charge separation, k_{CS}^S , calculated from the τ_f values were found to be 2.7×10^9 and 2.1×10^9 s $^{-1}$ and the quantum yields of charge-separation, Φ_{CS}^S , were found to be 0.79 and 0.75 (Table 1), respectively, indicating that efficient intramolecular charge separation occurs within $C_{60}(Gn-COOK)$; probably generating $C_{60}^{*-}(Gn-COO^{\bullet-})$.

Direct evidence for charge separation in the fullerodendrimers was obtained from nanosecond transient spectral studies which allowed us to verify the rate of charge recombination. The transient absorption spectra obtained by 532-nm laser-light irradiation are shown in Fig. 4. The spectrum at 12 ns after

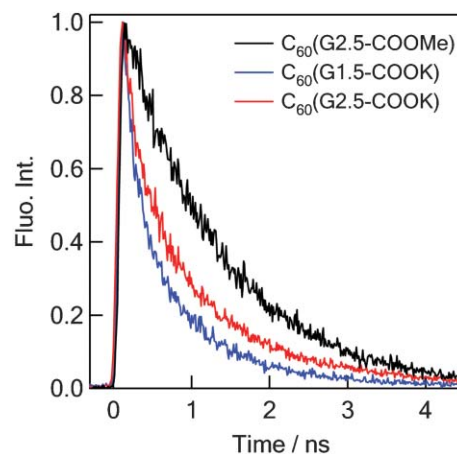


Fig. 3 Fluorescence time-profiles of $C_{60}(G1.5-COOK)$ and $C_{60}(G2.5-COOK)$ in H_2O and $C_{60}(G2.5-COOMe)$ in PhCN; $\lambda_{ex} = 400$ nm.

Table 1 Fluorescence lifetime (τ_f), charge-separation rate-constant (k_{CS}^S), charge-separation quantum yield (Φ_{CS}^S), charge-recombination rate constant (k_{CR}) and lifetime of the radical ion-pair (τ_{RIP}) in H_2O solution

Sample	τ_f /ps	k_{CS}^S /s $^{-1}$	Φ_{CS}^S	k_{CR} /s $^{-1}$	τ_{RIP} /ns
$C_{60}(G1.5-COOK)$	290	2.7×10^9	0.79	1.2×10^7	80
$C_{60}(G2.5-COOK)$	350	2.1×10^9	0.75	1.5×10^6	670

^a $k_{CS}^S = (1/\tau_f)_{COOK} - (1/\tau_f)_{COOMe}$; $\Phi_{CS}^S = [(1/\tau_f)_{COOK} - (1/\tau_f)_{COOMe}]/(1/\tau_f)_{COOK}$; $\tau_{f,COOMe} = 1400$ ps ($C_{60}(G2.5-COOMe)$ in PhCN).

laser-light exposure shows an absorption band of C_{60}^{*-} at 1020 nm, which exhibits initial fast decay and later slow decay as shown in the time profile shown in the inset at 1020 nm. In addition, broad bands were observed in the 600–1100 nm region probably attributable to the excited triplet state of C_{60} .

The rate of charge recombination, k_{CR} calculated by monitoring the decay of the 1020 band was found to be 1.2×10^7 s $^{-1}$ ($\tau_{RIP} = 80$ ns) from the initial decay. The longer time-scale measurement at 1020 nm (see ESI†) gave the k_{CR} value as 1.3×10^5 s $^{-1}$ ($\tau_{RIP} = 7700$ ns). In the case of $C_{60}(G2.5-COOK)$

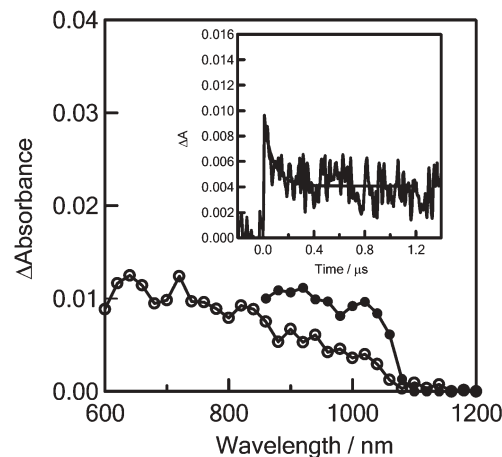


Fig. 4 Nanosecond transient absorption spectra of 0.1 mM $C_{60}(G1.5-COOK)$ in H_2O at 12 ns (●) and 1000 ns (○) after 532 nm laser-light irradiation. Inset: Time profile at 1020 nm.

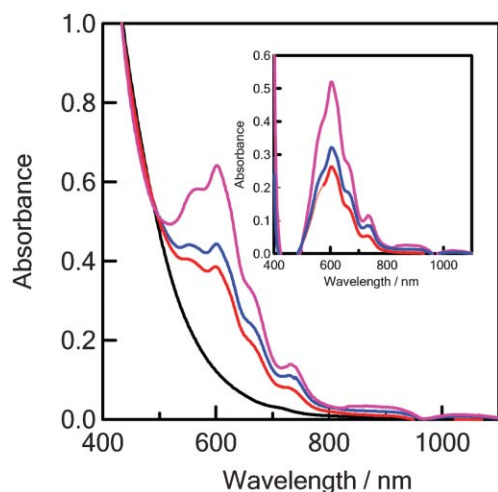


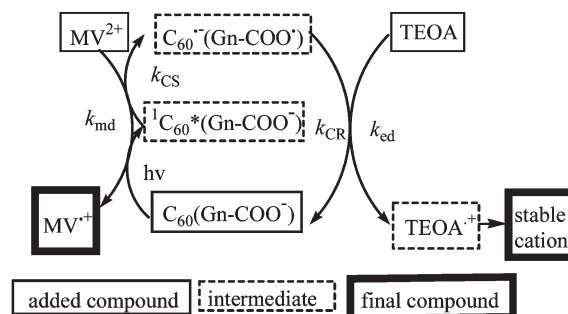
Fig. 5 Steady-state absorption spectra observed after 532-nm laser light irradiation of $C_{60}(G1.5-COOK)$ (0.1 mM) in the presence of MV^{2+} (1 (red), 2 (blue), 5 (pink) mM) and TEOA 5 mM) in deaerated aqueous solution. Inset: Subtracted absorption spectra of $C_{60}(G1.5-COOK)$ in each concentration.

from the decay time profile at 1020 nm, the k_{CR} was evaluated to be $1.5 \times 10^6 \text{ s}^{-1}$ ($\tau_{RIP} = 670 \text{ ns}$) and $1.0 \times 10^5 \text{ s}^{-1}$ ($\tau_{RIP} = 10000 \text{ ns}$) in H_2O . For these long-time measurements, contribution from second-order intermolecular events occurring in solution may be involved. In the case of $C_{60}(G2.5-COOK)$, the τ_{RIP} values are greater than those of $C_{60}(G1.5-COOK)$, suggesting that the steric interference of the larger poly(amidoamine), which separates the $C_{60}^{\bullet-}$ moiety from electron deficient COO^{\bullet} moieties.

In the presence of an excess of methyl viologen dication (MV^{2+}) and a sacrificial donor (triethanolamine = TEOA), a new absorption appeared in the steady-state absorption spectra after the laser-light irradiation of $C_{60}(G1.5-COOK)$ as shown in Fig. 5. A new absorption peak appeared at 600 nm with structures at 590, 660 and 720 nm and are all attributed to the radical cation of methyl viologen ($MV^{\bullet+}$). Similar spectral changes were observed for $C_{60}(G2.5-COOK)$. Without TEOA, on the other hand, no new absorption band appeared after the laser irradiation of $C_{60}(G1.5-COOK)$ and MV^{2+} .

In the transient absorption spectra observed by the photoexcitation of $C_{60}(G1.5-COOK)$ in the presence of MV^{2+} and TEOA, the absorption peak of $MV^{\bullet+}$ appeared at 620 nm (ESI†). The time profile at 620 nm shows both a rapid and slow rise; the rapid rise corresponds to the disappearance of the initial absorbance of $C_{60}^{\bullet-}$ at 1020 nm and the slow rise at 620 nm corresponds to the slow decay at 1020 nm. From the slow process, the rate constant for electron migration (k_{md}) from the $C_{60}^{\bullet-}$ moiety to MV^{2+} was evaluated to be $4.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for $C_{60}(G1.5-COOK)$. Similarly, the k_{md} value for $C_{60}(G2.5-COOK)$ was evaluated to be $2.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. In longer time scale measurements, the absorption of $MV^{\bullet+}$ was prolonged to more than 100 μs (see ESI†).

In summary, we have demonstrated a good example for a photoinduced charge-separation process of water-soluble fullerodendrimers with carboxylate ion at a terminal site, generating a



Scheme 1

unique charge-separated state, $C_{60}^{\bullet-} \sim COO^{\bullet}$, which persists over longer times than 80 ns. Thus, the electron in the C_{60} moiety migrates to the added MV^{2+} . On further addition of TEOA as sacrificial electron donor to COO^{\bullet} , steady-state concentration of $MV^{\bullet+}$, which has potential to transfer the electron to the electrode to generate electric current or to catalysts to split water generating hydrogen gas,¹¹ could be accumulated. These observations are summarized in Scheme 1, in which all the processes were confirmed, and their rate constants were evaluated by time-resolved measurements.

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