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Photoinduced Electron Transfer from Tetrathienylethylenes to Fullerenes (C_{60}/C_{70}): Tetrathienylethylene-Dendrimer Effect

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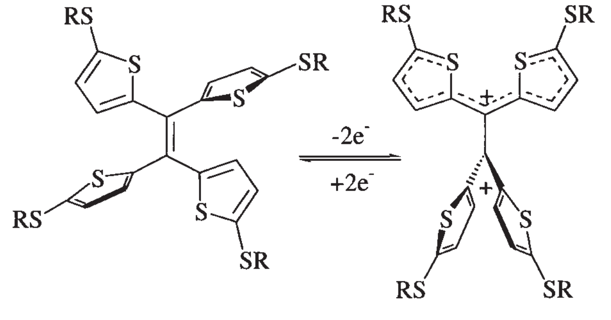
Photoinduced electron-transfer processes between C_{60}/C_{70} and tetrathienylethylenes (TTE's) in benzonitrile have been studied by measuring the transient absorption spectra in the Vis/NIR regions using nanosecond laser photolysis. The absorption bands of the radical anions of C_{60}/C_{70} ($C_{60}^{\bullet-}/C_{70}^{\bullet-}$) and radical cations of TTE's (TTE's$^{\bullet+}$) were observed with the decay of the triplet states of C_{60}/C_{70} ($^3C_{60}^*/^3C_{70}^*$), indicating that electron transfer takes place via $^3C_{60}^*/^3C_{70}^*$. In addition, formation of the dication of TTE (TTE^{2+}) was confirmed by its characteristic absorption band at 680 nm. The TTE^{2+} is formed by the stepwise collision of TTE with $^3C_{60}^*/^3C_{70}^*$. By the substitutions with the MeS groups at the thienyl rings of TTE, the efficiencies and rates of the electron-transfer processes became higher than those of TTE with the PhS groups. For dendrimer TTE's, the photoinduced electron-transfer processes also took place via $^3C_{60}^*/^3C_{70}^*$, although the efficiencies and rates were decreased with an increase in the dendrimer generation. After forward electron transfer, the back electron transfer processes were observed between separately solvated $C_{60}^{\bullet-}/C_{70}^{\bullet-}$ and TTE's$^{\bullet+}$ even for the dendrimer TTE's, which suggest that outer-sphere back electron-transfer took place in the backward processes.

Since the discovery of fullerenes[1] and their large-scale preparation,[2] their properties have been studied in various aspects for a decade.[3] Although photochemical properties also have been studied by many groups,[4–13] almost all photoinduced electron-transfer processes were reported on one-electron reduction process of fullerenes. On the other hand, electrochemical studies on C_{60} revealed the ability to receive up to six electrons.[14–17] Thus, photoinduced multiple-step electron-reduction processes of fullerenes are expected.

For the electron donors having two-electron oxidation ability, it would be expected that the two-electron-transfer processes take place by one-photon excitation of the electron acceptors with highly reduction abilities such as C_{60} and C_{70} in polar solvents. Fukuzumi et al. reported that one NADH (β-nicotinamide adenine dinucleotide) generates two $C_{60}^{\bullet-}$ by the successive reduction of the triplet state ($^3C_{60}^*$) and C_{60}.[18] The following reaction mechanism was revealed: NADH donates one electron to $^3C_{60}^*$, generating NADH$^{\bullet+}$ and $C_{60}^{\bullet-}$; the NADH$^{\bullet+}$ spontaneously donates hydrogen atom to $C_{60}^{\bullet-}$, yielding NAD$^+$ and HC_{60}^-, which changes into C_{60}^{2-} releasing H$^+$; reaction of C_{60}^{2-} with C_{60} leads to formation of two equivalents of $C_{60}^{\bullet-}$. Thus, the total process is irreversible.

In the present study, we employed tetrathienylethylene (TTE) derivatives as two-electron donors to achieve a reversible multi-step electron-transfer process (Scheme 1).[20] In neutral TTE's, π-orbitals of the diagonal two thiophene moieties are in the same plane as the ethylene π-orbital. The π-orbitals of the other two diagonal thiophenes are perpendicular to the ethylene π-orbital. Under the electrochemical or chemical oxidative condition, TTE's change easily to the dications (TTE^{2+}'s); thus, in the steady-state measurements, it is difficult to observe the cation radicals (TTE$^{\bullet+}$'s). The crystal structures of TTE^{2+}'s (Scheme 1) suggest that the origin of the stability of TTE^{2+}'s may be the delocalization of the ethylene cation over two vicinal thiophene rings in the same plane, which is perpendicular to the other thiophene rings.[20] These TTE's seem to be appropriate electron-donor molecules to investigate the two-electron oxidation processes with photoexcited states of C_{60} and C_{70}.



Scheme 1. Structure change of tetrathienylethylene (TTE) by two-electron oxidation.

Furthermore, we employed mainly TTE's with MeS substituents at 5-positions of the thiophene rings; the substituent effect was also investigated by replacing with PhS groups (Scheme 2). We also employed some TTE-dendrimers as

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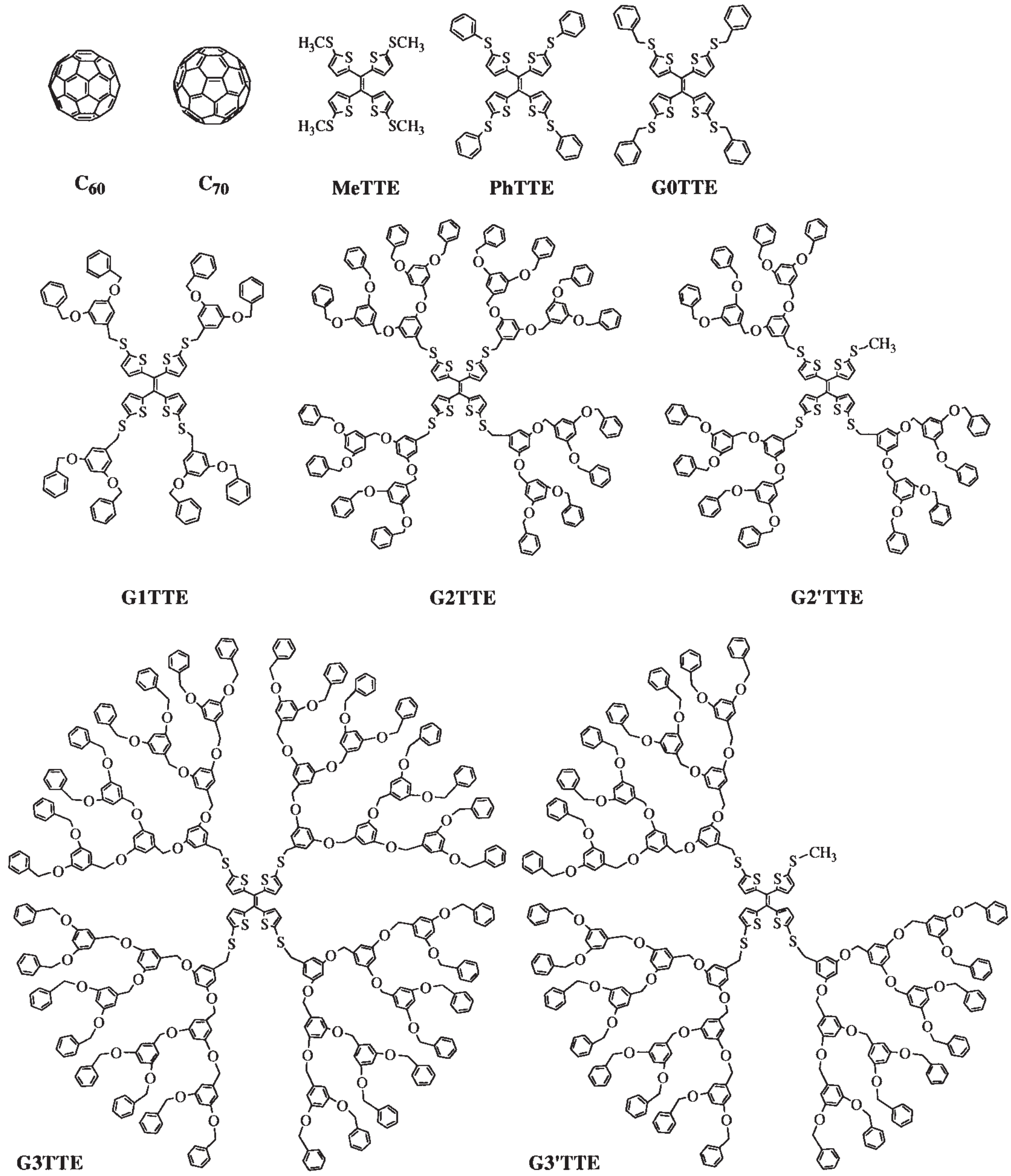


Scheme 2. Structures of fullerenes and TTE derivatives.

shown in Scheme 2 to investigate the dendrimer effects on the electron-transfer processes, because functions of dendrimers have attracted much attention in the fullerene chemistry including photochemistry.[21–32] For fullerenes modified by the dendrimer groups, interesting photochemical behavior including electron-transfer and energy-transfer processes has been reported.[25,30,31] In the mixture systems of fullerene and dendrimer, Kimura et al. reported specific interactions between C_{60} and dendric phenyl-substituted phthalocyanine in the ground and excited states.[32] In the present study, the effects of dendrimer groups of TTE's on the electron-transfer processes were disclosed on the basis of quantitative kinetic analyses.

Experimental

Materials. Buckminsterfullerene, C_{60} (+99.95%) and C_{70} (+99.8%) were obtained from Bucky-USA (Bellaire, TX). The TTE derivatives were prepared according to the methods described previously.[20] Benzonitrile and *s*-butyl chloride were purchased from Aldrich Chemical (Milwaukee, WI).

Measurements. The steady-state UV-visible absorption and fluorescence measurements were carried out with a JASCO/V-570 and a Shimadzu RF-5300PC, respectively, at room temperature. The absorption spectra of the cation radical and dication of TTE derivatives were obtained by γ-ray radiolysis using ^{60}Co in *s*-butyl chloride glassy matrix at 77 K.

Nanosecond transient absorption spectra in the Vis/NIR regions were measured by means of laser flash photolysis; OPO laser pumped by a Nd:YAG laser was used as the excitation source. For short timescale measurements, Si- or Ge-avalanche-photodiode module was used for detection of the monitoring light from a pulsed Xe lamp. For long timescale measurements, an InGaAs detector was employed for detection of the monitoring light from a continuous Xe lamp, as described in our previous reports.[33–41]

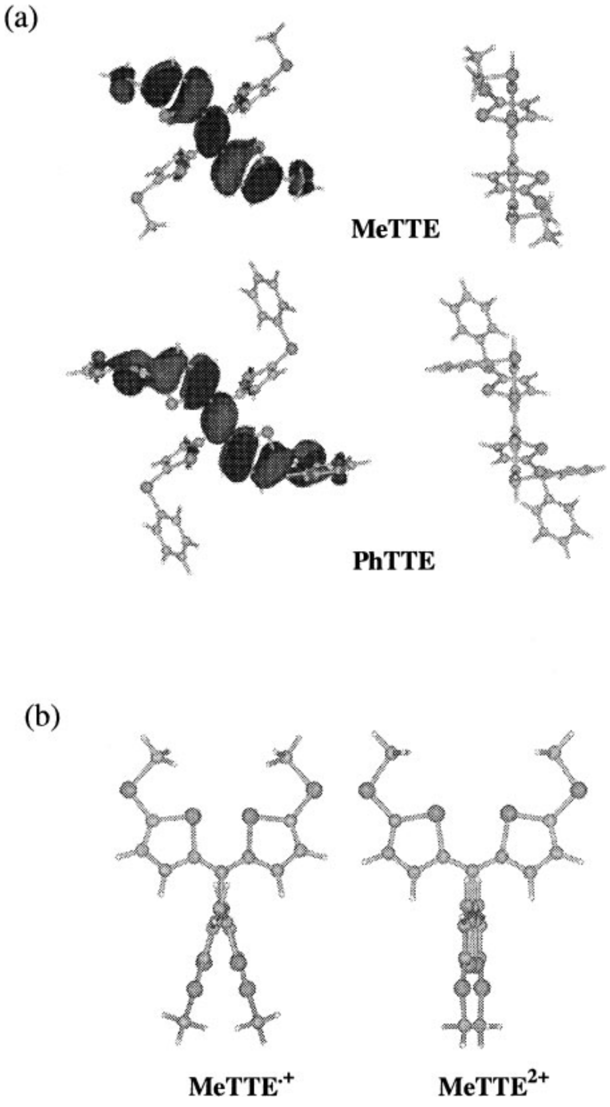


Fig. 1. Optimized structures and electron distributions of HOMO's calculated at B3LYP/3-21G level. (a) MeTTE and PhTTE, and (b) $MeTTE^{\bullet+}$ and $MeTTE^{2+}$.

Results and Discussion

MO Calculation. Optimized structures of MeTTE and PhTTE were calculated at B3LYP/3-21G level, as shown in Fig. 1(a). The electron density of the HOMO distributed on the two thiophene rings in the orthogonal position. These findings indicate that electron transfer takes place only when $^3C_{60}^*/^3C_{70}^*$ collide on one side of the thiophene plane. It is supposed that electron transfer does not occur so efficiently for PhTTE since steric hindrance by the PhS substituents is larger than that by the MeS substituents. In the case of G0TTE having benzyl-S substituents, however, electron transfer will be easy to occur compared with PhTTE because of small steric hindrance of the benzyl moiety.

Furthermore, optimized structures of $MeTTE^{\bullet+}$ and $MeTTE^{2+}$ are shown in Fig. 1(b). The structure of $MeTTE^{\bullet+}$ is similar to that of $MeTTE^{2+}$, but much different from that of neutral MeTTE. The MO calculation also revealed that $MeTTE^{\bullet+}$ is less stable than $MeTTE^{2+}$. These findings support the conclusion that $TTE^{\bullet+}$'s can change into TTE^{2+}'s easily.

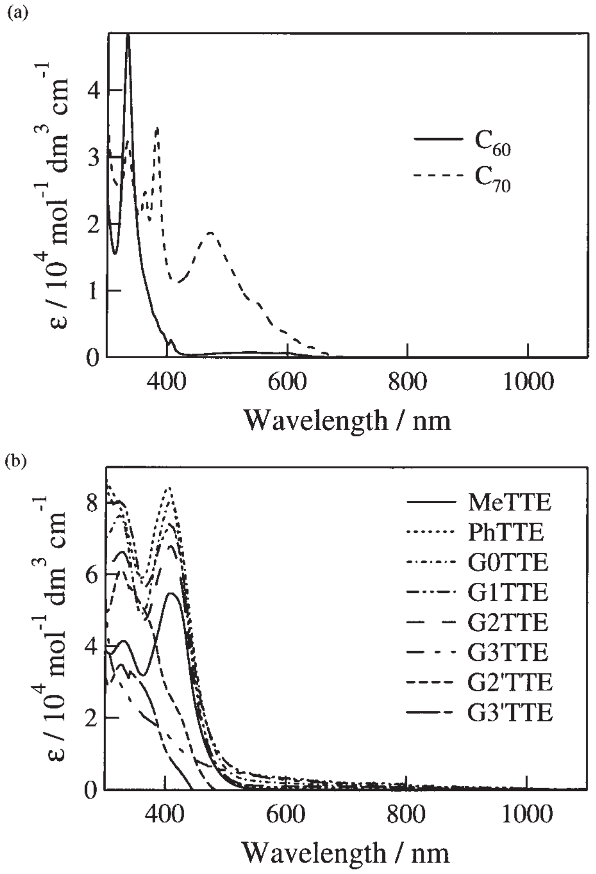


Fig. 2. Steady-state absorption spectra of (a) C_{60} and C_{70} and (b) TTE derivatives in benzonitrile.

Steady-State Absorption Spectra. Absorption spectra of C_{60}/C_{70} and TTE's in benzonitrile are shown in Fig. 2. With an increase of the generation of the dendritic groups, the absorption maximum around 400 nm shifts to shorter wavelengths. Furthermore, for G3TTE and G3′TTE, the absorption bands around 400 nm almost disappeared. These findings indicate that the TTE unit at the core was distorted by the substitutions with large dendrimer groups until the π-conjugation of the TTE core is considerably decreased. However, the difference of absorption spectra between G2′TTE and G3′TTE is small, indicating that the structure of TTE unit in G3′TTE is similar to that of G2′TTE.

In the laser flash photolysis experiments in the present paper, excitation of C_{60} and C_{70} was carried out with the 600 nm laser light in the presence of TTE's. For the TTE derivatives having the absorption tails at 600 nm, the TTE derivatives may be also excited at the same time; however, excitation of TTE derivatives with the 600-nm nanosecond laser in benzonitrile did not give appreciable transient absorption bands, showing that photo-ejection of electrons does not occur.

Absorption Spectra of Cations of Tetrathienylethylenes. Absorption spectra of oxidized MeTTE were measured by stepwise addition of $FeCl_3$ in benzonitrile.[42,43] With consumption of neutral molecules, a new absorption band appeared at 675 nm (Fig. 3), which can be attributed to the absorption of

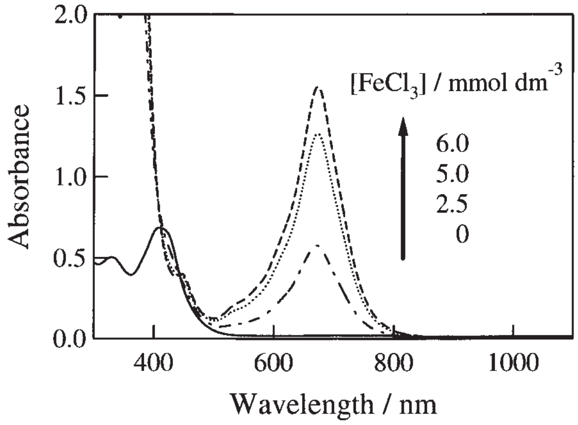


Fig. 3. Spectral changes upon stepwise oxidation of MeTTE (0.1 mmol dm^{-3}) by adding $FeCl_3$ in benzonitrile.

Table 1. Absorption Maxima (λ_{max}) and Molar Extinction Coefficients (ε_{max}) of TTE^{2+}s

Compound	λ_{max}/nm	ε_{max}/mol^{-1} dm^3 cm^{-1}
MeTTE	675	1.1×10^5
PhTTE	682	9.3×10^4
G0TTE	684	1.1×10^5
G1TTE	690	9.5×10^4
G2TTE	691	4.7×10^4
G3TTE	693	7.1×10^3
G2′TTE	686	5.4×10^4
G3′TTE	686	2.9×10^4

the dication of MeTTE ($MeTTE^{2+}$). The $MeTTE^{\bullet+}$ did not appear because $MeTTE^{\bullet+}$ was oxidized easily to generate $MeTTE^{2+}$ by $FeCl_3$, even under the condition of [MeTTE] $\gg$ [$FeCl_3$] ([compound] denotes concentration of compound). Oxidation processes generating dications were confirmed for other TTE's. The absorption peaks and molar extinction coefficients (ε) of dications of TTE's are summarized in Table 1.

An absorption spectrum of MeTTE after γ-ray irradiation in *s*-butyl chloride at 77 K is shown in Fig. 4. New absorption bands appeared around 680 and 1090 nm. The 680-nm band was assigned to $MeTTE^{2+}$, while the 1090-nm band may be attributed to $MeTTE^{\bullet+}$.

Fullerene Excitation in Mixture System. By the excitation of C_{60} with the 600-nm laser light in the presence of MeTTE in benzonitrile, transient absorption spectra were observed as shown in Fig. 5(a). In the spectrum at 100 ns after the nanosecond laser pulse, the 740-nm band was assigned to $^3C_{60}^*$.[4,5,7,9,42,43] With the decay of $^3C_{60}^*$, new absorption bands appeared at 680 and 1080 nm; the 1080-nm band was attributed to both $C_{60}^{\bullet-}$ and $MeTTE^{\bullet+}$, whose bands may be accidentally overlapped.[11,44] The 680-nm band was attributed to $MeTTE^{2+}$. In the time profiles in Fig. 5(a), it is apparent that the decay of $^3C_{60}^*$ is almost a mirror image of the rises of $C_{60}^{\bullet-}$ and $MeTTE^{\bullet+}$, indicating that electron transfer takes place via $^3C_{60}^*$.[11]

A more clear transient absorption band of $MeTTE^{\bullet+}$ was observed for the system of MeTTE with C_{70}, as shown in Fig. 5(b). With the decay of $^3C_{70}^*$ at 980 nm, absorption bands of $MeTTE^{2+}$, $MeTTE^{\bullet+}$, and $C_{70}^{\bullet-}$ appeared at 680, 1080, and 1380 nm, respectively.[43] The ε value of $MeTTE^{\bullet+}$ was calculated to be 8800 mol^{-1} dm^3 cm^{-1} using the ε values of $C_{70}^{\bullet-}$ and $MeTTE^{2+}$. From these ε values and the observed absorbance, the concentration of $MeTTE^{2+}$ was evaluated to be about 5% of $MeTTE^{\bullet+}$.

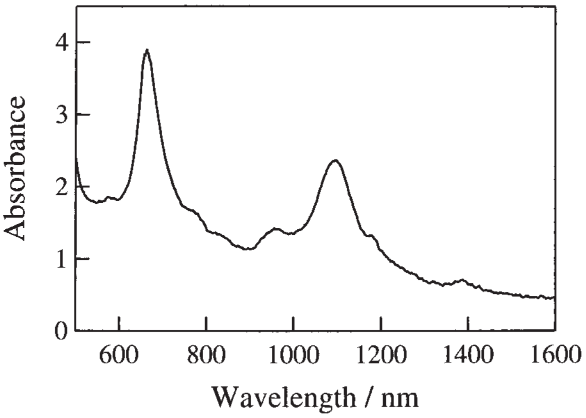


Fig. 4. Steady-state absorption spectrum of MeTTE (0.1 mmol dm^{-3}) after γ-ray irradiation in *s*-butyl chloride rigid glass at 77 K.

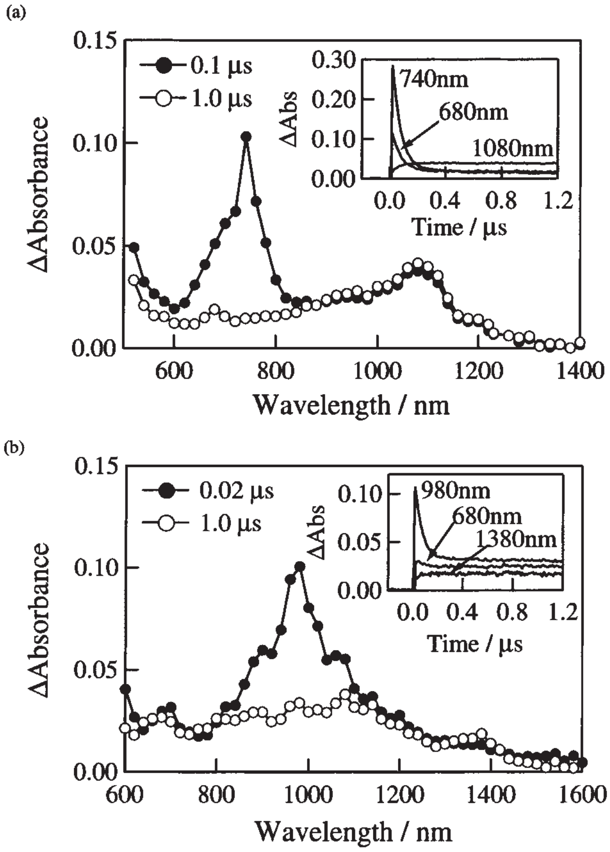


Fig. 5. Transient absorption spectra observed by 600-nm laser irradiation of (a) C_{60} (0.1 mmol dm^{-3}) and (b) C_{70} (0.1 mmol dm^{-3}) in the presence of MeTTE (5 mmol dm^{-3}) in benzonitrile. Inset: Time profiles.

The electron-transfer mechanism which generates $MeTTE^{2+}$ was investigated by measurements of the transient absorption intensity of $MeTTE^{2+}$ at 680 nm with changing

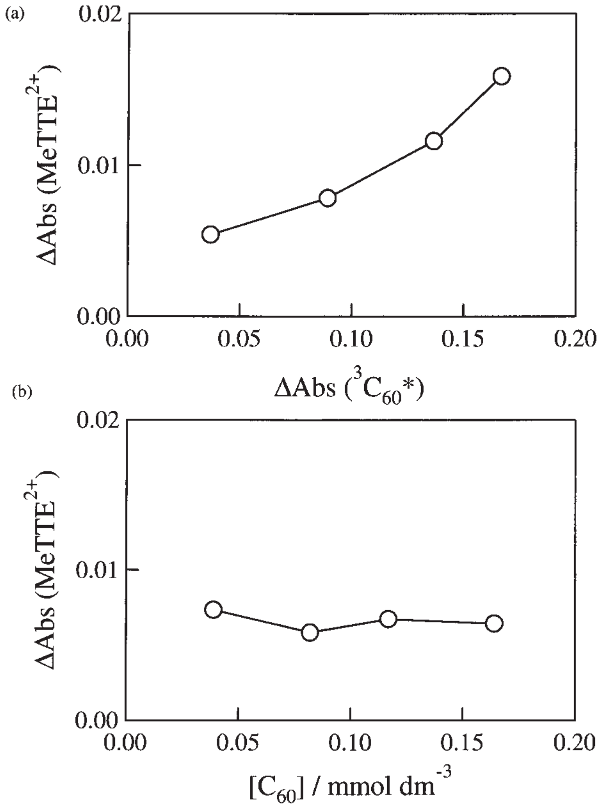


Fig. 6. Comparison of Δabsorbance of MeTTE^{2+} (a) by changing concentration of $^3\mathrm{C}_{60}{}^*$ under the same concentration of C_{60} and MeTTE and (b) by changing concentration of C_{60} under the same concentration of $^3\mathrm{C}_{60}{}^*$ and MeTTE in benzonitrile.

concentration of $^3\mathrm{C}_{60}{}^*$ and C_{60}. Results appear in Figs. 6(a) and 6(b), respectively. Absorption of MeTTE^{2+} increased only when the concentration of $^3\mathrm{C}_{60}{}^*$ was increased by changing the laser power while keeping [MeTTE] and $[\mathrm{C}_{60}]$ constant. On the other hand, the amount of MeTTE^{2+} is independent of $[\mathrm{C}_{60}]$. These findings suggest that additional electron transfer takes place from $\mathrm{MeTTE}^{\bullet+}$ to $^3\mathrm{C}_{60}{}^*$: in other words, that MeTTE reacts with two $^3\mathrm{C}_{60}{}^*$ to give MeTTE^{2+} as shown in Scheme 3. The formation process of MeTTE^{2+} via the collision between $\mathrm{MeTTE}^{\bullet+}$ and C_{60} may be impossible, because the electron-acceptor ability of C_{60} is weaker than that of $^3\mathrm{C}_{60}{}^*$.

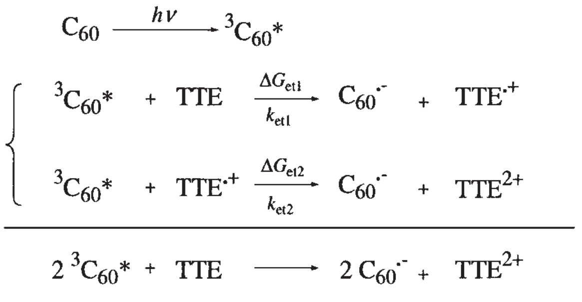
In the cases of other TTE's, similar transient absorption spectra were observed in the presence of C_{60} and C_{70}, indicating that electron transfer also takes place. With increase in the generation of dendrimer groups, the rate constants of the processes decreased, as discussed in the later section. Thus, the formation of dication was decreased. In Scheme 3, since the free-energy change of the first electron transfer (ΔG_{et1}) is evaluated to be negative using the observed oxidation potential, one electron-transfer process is expected easily to occur. ΔG_{et1} can be expressed by the Rehm-Weller equation as Eq. 1:[45]

$$\Delta G_{\mathrm{et1}} = E_{\mathrm{ox}}{}^1 - E_{\mathrm{red}} - E_{\mathrm{T}} - e_0{}^2/\varepsilon_{\mathrm{S}} d_{\mathrm{CC}} \tag{1}$$

where $E_{\mathrm{ox}}{}^1$, E_{red}, E_{T}, and $e_0{}^2/\varepsilon_{\mathrm{S}} d_{\mathrm{CC}}$ are the one-electron oxidation potential of the donor (TTE), the reduction potential of the acceptor (C_{60}, C_{70}), the triplet energy of the exciting species ($^3\mathrm{C}_{60}{}^*$, $^3\mathrm{C}_{70}{}^*$), and the Coulomb attraction energy, respectively. For evaluation of the free-energy change of the second-step electron transfer (ΔG_{et2}), we need the value of the oxidation potential from $\mathrm{MeTTE}^{\bullet+}$ to MeTTE^{2+}. ΔG_{et2} also can be expressed as Eq. 2:

$$\Delta G_{\mathrm{et2}} = E_{\mathrm{ox}}{}^2 - E_{\mathrm{red}} - E_{\mathrm{T}} - e_0{}^2/\varepsilon_{\mathrm{S}} d_{\mathrm{CC}} \tag{2}$$

where $E_{\mathrm{ox}}{}^2$ is the second-electron oxidation potential of the donor (TTE). According to previous literature,[20] the cyclic voltammetry curve of MeTTE shows one-wave two-electron oxidation. The oxidation potential of $\mathrm{MeTTE}^{\bullet+}$ ($E_{\mathrm{ox}}{}^2$) may be hidden in this peak. If the $E_{\mathrm{ox}}{}^2$ is same as $E_{\mathrm{ox}}{}^1$, the second-step electron transfer is also exothermic, producing MeTTE^{2+} efficiently. These processes are quite similar to those reported for a donor-acceptor-donor triad, in which the two photoexcited donors donate two electrons to the central acceptor successively.[46]



Scheme 3. Electron-transfer mechanisms.

As another possible process for the production of MeTTE^{2+}, the disproportionation process in which collision of two $\mathrm{MeTTE}^{\bullet+}$ yields MeTTE^{2+} and MeTTE, may be considered. If disproportionation occurs, MeTTE^{2+} would be observed after the decay of $\mathrm{MeTTE}^{\bullet+}$. As seen in Figs. 4 and 5, however, we can observe the MeTTE^{2+} at the same time of $\mathrm{MeTTE}^{\bullet+}$; thus, the disproportionation process can be excluded.

Quantum Yields and Electron-Transfer Rates. The efficiency of electron transfer can be calculated from the ratio of the maximal concentration of the generated radical ions to the

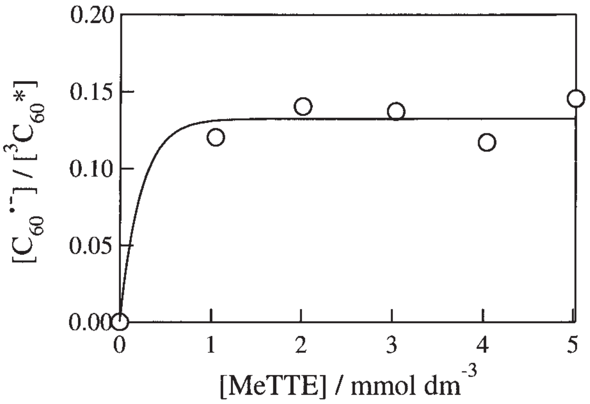


Fig. 7. Plots of $[\mathrm{C}_{60}{}^{\bullet-}]_{\mathrm{max}}/[^3\mathrm{C}_{60}{}^*]_{\mathrm{max}}$ against [MeTTE] for electron transfer via $^3\mathrm{C}_{60}{}^*$.

initial concentration of the triplet states of fullerenes.[43,47,48] For example, the ratios of $[C_{60}^{\bullet-}]_{max}/[^3C_{60}^*]_{max}$ are plotted against the concentration of MeTTE as shown in Fig. 7, in which the observed absorbance at 1080 nm was corrected by the ε value of MeTTE$^{\bullet+}$. The value of $[C_{60}^{\bullet-}]_{max}/[^3C_{60}^*]_{max}$ is a function of the initial concentration of TTE as shown in Eq. 3:

$$[C_{60}^{\bullet-}]_{max}/[^3C_{60}^*]_{max} = k_{et}[\mathrm{TTE}]_0/\{k_T{}^0 + k_q[\mathrm{TTE}]_0\} \tag{3}$$

where $k_T{}^0$, k_q, and k_{et} are decay rate of $^3C_{60}^*$ in the absence of TTE, the bimolecular quenching rate constant of $^3C_{60}^*$ by TTE, and electron transfer rate constant, respectively.[6,11,43,44] The k_q value can be evaluated from the dependence of the first-order decay rate of $^3C_{60}^*$ (Fig. 8) on the concentration of TTE, as summarized in Table 2. When $k_T{}^0 \ll k_q[\mathrm{TTE}]_0$, the $[C_{60}^{\bullet-}]_{max}/[^3C_{60}^*]_{max}$ value takes a constant value at high $[\mathrm{TTE}]_0$ range as shown in Fig. 7. Therefore, the saturated value is regarded as the quantum yield of electron transfer (Φ_{et}) via $^3C_{60}^*$.[47] Finally, the k_{et} value can be obtained from the relation: $k_{et} = k_q \times \Phi_{et}$.[13,43,47] The Φ_{et} values for the reactions via $^3C_{70}^*$ were also evaluated similarly. In Table 2, the k_{et}, k_q, and Φ_{et} values for C_{60} show almost the same tendency as the corresponding values of C_{70} with the change of TTE's.

Back Electron Transfer. The absorbance of the radical ion begins to decrease after reaching a maximum, as shown in the inset of Fig. 9. The decay of the radical ion can be attributed to the back electron transfer, because appreciable evidence for some other reaction pathway was not confirmed in the steady-state absorption of the solution after the laser experiments. The decay-time profile of the radical ion obeys second-order kinetics (Fig. 9), indicating that each radical ion is solvated as a free radical ion. The slope of the linear line corresponds to $2k_{bet}/\varepsilon$. On substituting the reported ε values, we evaluated the k_{bet} values as listed in Table 2. The k_{bet} values are all close to the diffusion-controlled limit ($k_{diff} = 5.3 \times 10^9$ mol^{-1} dm^3 s^{-1} in benzonitrile),[49] which supports the conclusion that the back electron-transfer process is exothermic, as anticipated from the negative free-energy change.[50,51] Since the concentration of MeTTE^{2+} is far lower than [MeTTE$^{\bullet+}$], the presence of MeTTE^{2+} does not affect the decay kinetics of [MeTTE$^{\bullet+}$] and $[C_{60}^{\bullet-}]$ much. The decay of

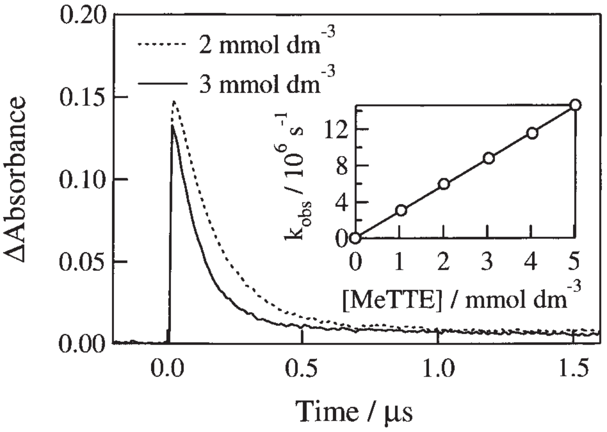


Fig. 8. Decays of $^3C_{60}^*$ in the presence of MeTTE in benzonitrile. Inset: Pseudo-first-order plot.

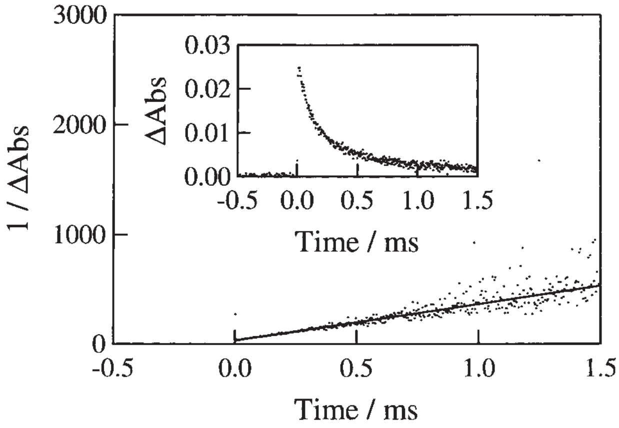


Fig. 9. Second-order plot for the decay of $C_{60}^{\bullet-}$ and MeTTE$^{\bullet+}$ at 1080 nm in benzonitrile. Inset: Time profile.

Table 2. Rate Constants (k_q), Quantum Yields (Φ_{et}), and k_{et} ($= k_q \times \Phi_{et}$) Values for Electron Transfer via $^3C_{60}^*/^3C_{70}^*$ and Back Electron-Transfer Rate Constants (k_{bet}) in Benzonitrile

Donor	Acceptor	$k_q/10^9$ mol^{-1} dm^3 s^{-1}	Φ_{et}	$k_{et}/10^8$ mol^{-1} dm^3 s^{-1}	$k_{bet}/10^9$ mol^{-1} dm^3 s^{-1}
MeTTE	$^3C_{60}^*$	2.9	0.14	4.1	3.5
PhTTE	$^3C_{60}^*$	1.5	0.017	0.26	—
G0TTE	$^3C_{60}^*$	1.8	0.054	0.97	6.7
G1TTE	$^3C_{60}^*$	1.4	0.071	0.99	4.2
G2TTE	$^3C_{60}^*$	0.37	0.097	0.36	4.5
G3TTE	$^3C_{60}^*$	0.093	0.053	0.049	3.6
G2′TTE	$^3C_{60}^*$	0.75	0.16	1.2	3.6
G3′TTE	$^3C_{60}^*$	0.36	0.097	0.35	2.0
MeTTE	$^3C_{70}^*$	3.1	0.27	8.4	2.6
PhTTE	$^3C_{70}^*$	1.7	0.041	0.70	—
G0TTE	$^3C_{70}^*$	2.0	0.11	2.2	3.1
G1TTE	$^3C_{70}^*$	1.5	0.13	2.0	2.5
G2TTE	$^3C_{70}^*$	0.53	0.14	0.74	3.0
G3TTE	$^3C_{70}^*$	0.11	0.087	0.096	2.3
G2′TTE	$^3C_{70}^*$	0.85	0.17	1.4	1.7
G3′TTE	$^3C_{70}^*$	0.53	0.16	0.85	1.3

$MeTTE^{2+}$ was also observed after reaching the maximum. $MeTTE^{2+}$ may decay under the condition of $[MeTTE^{2+}] \ll [C_{60}^{\bullet -}]$; in this case, back electron transfer may take place stepwise.

Substituent Effect. For both C_{60} and C_{70}, the k_q values of PhTTE are small (ca. 1/2) compared with those of MeTTE, which reflects the higher oxidation potential of PhTTE (0.86 V vs SCE) than MeTTE (0.73 V vs SCE) by 0.13 V.[20] The change in oxidation potential and k_q values can be attributed to the difference in the inductive effect between the MeS and PhS groups; the MeS group has higher electron-donating ability than PhS group.[52] The Φ_{et} values of PhTTE, however, are smaller than those of MeTTE (1/7). Usually, the Φ_{et} values are determined by the dissociation of the collision complex (triplet exciplex) into the radical ions;[13,43,47] thus, deactivation processes without electron transfer reduce the Φ_{et} values. Such a large difference in the Φ_{et} values perhaps suggests some structural changes in the encounter complex, in which dissociation into the radical ions easily occurs for MeTTE, while deactivation processes predominantly occur for PhTTE. In the triplet exciplex, the PhS group may inhibit the dissociation into the radical ions. Because of small k_q and Φ_{et}, the k_{et} values of PhTTE are smaller than those of MeTTE by a factor of 1/12–1/16. The steric hindrance by the PhS groups also results in such a big difference in the Φ_{et} and k_{et} values between MeTTE and PhTTE.

Dendrimer Effect. For both $^3C_{60}{}^*$ and $^3C_{70}{}^*$, the k_q values of dendrimer TTE's decrease with the generation; the decrease in the k_q values on going from MeTTE to G0TTE and G1TTE is rather small (ca. 1/2), whereas a drastic decrease (ca. 1/15) was observed from G1TTE to G2TTE and G3TTE. This finding indicates that the frequency factor for collision of the TTE core and $^3C_{60}{}^*/^3C_{70}{}^*$ is much decreased by the increase in the dendrimer generation, because the collision of $^3C_{60}{}^*/^3C_{70}{}^*$ with the dendrimer group (the phenyl ether moieties) does not quench $^3C_{60}{}^*/^3C_{70}{}^*$. This implies that outer-sphere electron transfer takes place, but penetration of $^3C_{60}{}^*/^3C_{70}{}^*$ into the dendrimers seems not to take place. On the other hand, the k_q values of G2′TTE and G3′TTE are larger than those of G2TTE and G3TTE by factors of 2–5. This indicates that G2′TTE and G3′TTE have enough space for $^3C_{60}{}^*$ and $^3C_{70}{}^*$ to attain close proximity to core TTE in G2′TTE and G3′TTE.

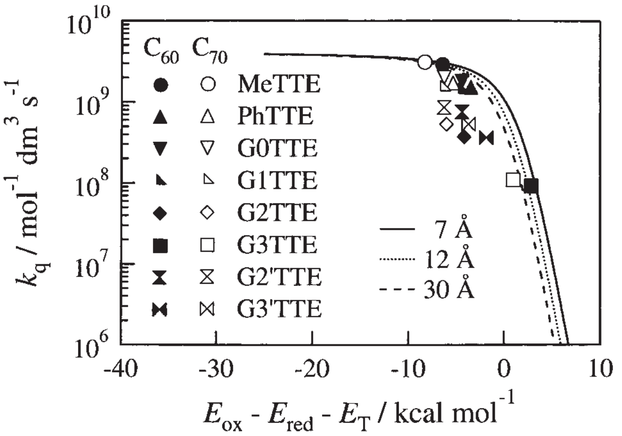


Fig. 10. Plots of k_q against $(E_{ox} - E_{red} - E_T)$ for electron transfer via $^3C_{60}{}^*$ (filled marks) or $^3C_{70}{}^*$ (open marks). Three lines were calculated from the Rehm-Weller equation (4).

Table 3. Redox Potentials (E) of TTE's and Fullerenes

Compound	E_{ox}/V[a)]	E_{red}/V[a)]
MeTTE	+0.73	—
PhTTE	+0.86	—
G0TTE	+0.82	—
G1TTE	+0.82	—
G2TTE	+0.83	—
G3TTE	+1.13	—
G2′TTE	+0.82	—
G3′TTE	+0.93	—
C_{60}	—	−0.56
C_{70}	—	−0.51

a) vs SCE.

In Fig. 10, the k_q values are plotted against $(E_{ox} - E_{red} - E_T)$ values, which correspond to the free energy change without Coulombic term. The k_q values are expressed as Eqs. 4 and 5:[48,50,51]

$$k_q = k_{diff}/[1 + A\{\exp(\Delta G^{\neq}/RT) + \exp(\Delta G/RT)\}] \quad (4)$$

$$\Delta G^{\neq} = \{(\Delta G/2)^2 + (\Delta G^{\neq}{}_0)^2\}^{1/2} + \Delta G/2 \quad (5)$$

where A, $\Delta G^{\neq}$, $\Delta G^{\neq}{}_0$, R, and T are preexponential factor ($A = 0.25$), activation free energy, activation free energy at $\Delta G = 0$ ($\Delta G^{\neq}{}_0 = 2.4$ kcal mol^{-1}), gas constant, and absolute temperature, respectively. The $(E_{ox} - E_{red} - E_T)$ values are calculated by Eq. 1, using redox potentials of TTE's and fullerenes as summarized in Table 3.[20] By changing the encounter distance, the calculated curve by Eq. 4 changes as indicated in Fig. 10; this suggests long-range electron-transfer processes (>30 Å). These findings indicate that the size of dendrimer moiety of the 3rd generation is so large that electron transfer rates decrease to a large extent: this is a dendrimer effect.

The Φ_{et} values are almost constant for G0TTE, G1TTE, G2TTE, and G3TTE; on the other hand, the Φ_{et} values of G2′TTE and G3′TTE are almost twice the values of G2TTE and G3TTE, respectively. This finding indicates that $^3C_{60}{}^*$ or $^3C_{70}{}^*$ entering into the pocket of the dendrimer TTE's surely accepts an electron from the TTE core, because the pocket sizes of the dendrimer TTE's do not change so much with the generation of dendrimers.

Finally, the k_{et} values of dendrimer TTE's decrease with increasing the generation of the dendrimers. The k_{et} values are one order smaller than the k_q values, since the Φ_{et} values are almost 0.1. Back electron transfer with dendrimers also obeys second-order kinetics, suggesting outer-sphere back electron transfer, even in the dendrimers of the higher generation. These k_{bet} values are close to the k_{diff} value and did not change much with the dendrimer generation, because of sufficiently negative ΔG_{bet} values. For such systems, back electron transfer between oppositely charged species takes place for long distances.

Conclusion

The present study shows that electron transfer takes place via triplet excited fullerenes in the presence of TTE in benzonitrile. In addition to the one-electron oxidation of MeTTE, MeTTE^{2+} was produced by the successive collision of the triplet-excited fullerenes with MeTTE$^{\bullet+}$, although the possibility is not high. A significant substituent effect was observed between the –SMe and –SPh groups. The k_q and k_{et} values decreased with an increase of the generation of the dendrimer groups, while relatively small changes were observed for Φ_{et}. The back electron transfer takes place via second-order kinetics, suggesting that the radical ions are separately solvated. The k_{bet} values are all close to the k_{diff} value, although the k_{et} values are less than the k_{diff} value by factors of 1/10–1/100.

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