Photoinduced electron transfer from tetraethoxyethene to C_{60} and C_{70} studied by laser flash photolysis

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The electron transfer from tetraethoxyethene (TEOE), which has high electron-donor ability, to photoexcited C_{60} or C_{70} in polar and less polar solvents has been investigated by 532 nm laser flash photolysis with observation of the transient absorption bands in the near-IR region. The transient absorption bands of the triplet states of fullerenes (${}^{T}C_{60}{}^{*}$ and ${}^{T}C_{70}{}^{*}$), which appeared immediately after nanosecond laser exposure, were effectively quenched by TEOE. With the decay of ${}^{T}C_{60}{}^{*}$ and ${}^{T}C_{70}{}^{*}$, the absorption bands of $C_{60}{}^{\cdot -}$ and $C_{70}{}^{\cdot -}$ appeared at 1070 and 1380 nm, respectively, showing that the electron transfer takes place from TEOE to ${}^{T}C_{60}{}^{*}$ or to ${}^{T}C_{70}{}^{*}$. Then, $C_{60}{}^{\cdot -}$ and $C_{70}{}^{\cdot -}$ disappear by back electron transfer to $TEOE^{\cdot +}$. The efficiencies and rates of the electron-transfer reactions vary with solvent polarity.

Introduction

It has been reported that photoexcited fullerenes such as C_{60} and C_{70} act as good electron acceptors in the presence of electron donors such as aromatic amines and aliphatic amines.[1–8] Recently, it has been reported that organic compounds with a C=C bond add to the triplet state of C_{60} (${}^{T}C_{60}{}^{*}$);[9,10] the reaction mechanism was presumed to proceed *via* photoinduced electron transfer between the triplet state of ${}^{T}C_{60}{}^{*}$ and olefins forming the radical anion and radical cations, respectively. However, the direct detection of the ion radicals has not been performed yet for such reaction systems.

In the case of C_{60} or C_{70}, the initial steps of the photoinduced electron-transfer reactions have been investigated by photochemical techniques such as transient absorption spectroscopy by measuring the quenching rates of ${}^{T}C_{60}{}^{*}$ and ${}^{T}C_{70}{}^{*}$ in the visible region.[4,5] By these methods, it was found that the electron transfer takes place *via* ${}^{T}C_{60}{}^{*}$ and ${}^{T}C_{70}{}^{*}$ forming their radical anions ($C_{60}{}^{\cdot -}$ and $C_{70}{}^{\cdot -}$). These short-lived intermediates show their transient absorption bands at longer wavelength than the visible region.[11–15]

Thus, in this study, we observed the transient absorption spectra in the near-IR region to confirm the electron transfer of these fullerenes with olefins. As olefin, we employed tetraethoxyethene [$(C_2H_5O)_2C{=}C(OC_2H_5)_2$; abbreviated to TEOE], since this olefin is known as a good electron donor.[16–18] The photochemical and thermal reaction products between TEOE and C_{60} (or C_{70}) were recently reported by Zhang *et al.*[19,20] Both C_{60} and C_{70} were used to examine which is the more powerful electron acceptor. Reaction media may play an important role in the photoinduced electron transfer and adduct formation.[3,5,21,22]

Results and discussion

Steady-state UV–VIS spectra

The steady-state absorption spectrum of C_{60} and TEOE in benzonitrile was recorded between 400 and 800 nm as shown in Fig. 1. TEOE has no absorption at 532 nm, which allows the use of laser light at 532 nm for excitation of fullerenes only. The absorption spectrum of the mixture of C_{60} and TEOE in benzonitrile (Fig. 1) is a superposition of the components, suggesting that no appreciable interaction exists between C_{60} and TEOE in the ground states under the concentration conditions employed by the laser photolysis experiments in this study ($<1.0 \times 10^{-2}$ mol dm^{-3} of TEOE).[2,23] The absorption bands of the components are not appreciably affected by solvent polarity. Similarly, a lack of specific interaction between C_{70} and TEOE was shown in absorption spectra.

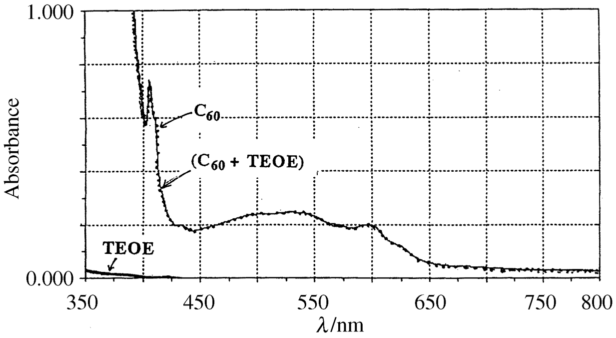

Fig. 1 Steady UV–VIS spectra of C_{60} (——, 2.5×10^{-4} mol dm^{-3}), TEOE (——, 1.0×10^{-2} mol dm^{-3}) and their mixture (·····) in benzonitrile

Transient spectra

Fig. 2 shows the transient absorption spectra in the near-IR region obtained by the laser flash photolysis of C_{60} with 532 nm light in the presence of TEOE (1.0×10^{-2} mol dm^{-3}) in benzonitrile. The transient absorption band at 740 nm appearing immediately after nanosecond laser exposure is attributed to the triplet–triplet absorption band of ${}^{T}C_{60}{}^{*}$.[24–28] With the decay of ${}^{T}C_{60}{}^{*}$, new absorption bands appeared in the region of 950–1100 nm. The absorption band at 1070 nm with a shoulder at 950 nm is a characteristic absorption of $C_{60}{}^{\cdot -}$.[29]

The observed time-profiles of the absorption bands are shown in the insert of Fig. 2. The decay of ${}^{T}C_{60}{}^{*}$ at 740 nm, which did not show appreciable decay during 1 μs without TEOE, was accelerated in the presence of TEOE (10^{-2} mol dm^{-3}). Accompanied by the decay of ${}^{T}C_{60}{}^{*}$, the absorption intensity of $C_{60}{}^{\cdot -}$ at 1070 nm increased reaching a maximum at

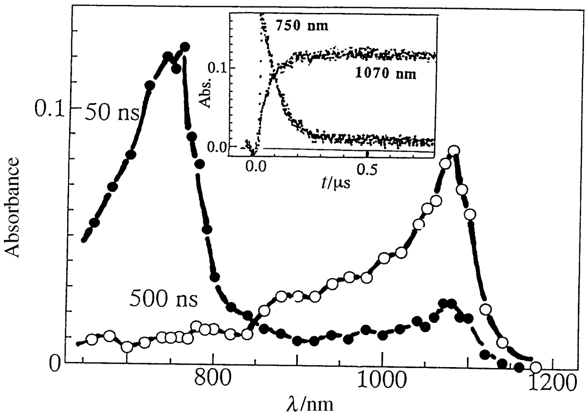

Fig. 2 Transient absorption spectra obtained by 532 nm laser flash photolysis of C_{60} (2.5×10^{-4} mol dm^{-3}) in the presence of TEOE (1.0×10^{-2} mol dm^{-3}) in deaerated benzonitrile; (●) 50 ns and (○) 500 ns. Insert: time profiles at 750 nm and 1070 nm.

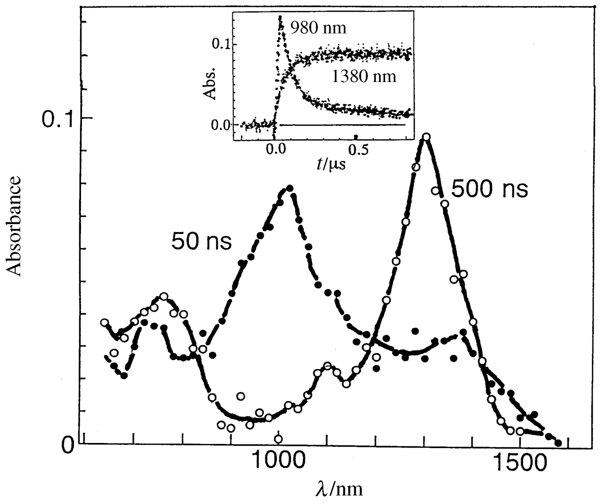

Fig. 3 Transient absorption spectra obtained by 532 nm laser flash photolysis of C_{70} (2.5×10^{-4} mol dm^{-3}) in the presence of TEOE (1.0×10^{-2} mol dm^{-3}) in deaerated benzonitrile. (●) 50 ns and (○) 500 ns. Insert: time profiles at 980 and 1380 nm.

ca. 150 ns; then, it began to decay gradually in *ca.* 10 μs. From the rise and decay, it is evident that $C_{60}^{\bullet -}$ is produced *via* ${}^{T}C_{60}^{*}$ which accepts an electron from TEOE.

Transient absorption spectra for C_{70}–TEOE in benzonitrile obtained by the exposure of the pulsed 532 nm laser light are shown in Fig. 3. Immediately after the nanosecond laser pulse at 532 nm, the absorption band of ${}^{T}C_{70}^{*}$ appeared at 980 nm with a shoulder at 720–730 nm.[30,31] The main absorption at 980 nm was quenched by the addition of TEOE, and the absorption band of $C_{70}^{\bullet -}$ appeared at 1380 nm with a shoulder at 750 nm.[12,32,33] As shown in the inserted time-profile, the absorption intensity of ${}^{T}C_{70}^{*}$ at 980 nm, which did not show appreciable decay for 1 μs in the absence of TEOE, decayed rapidly. The rise of the absorption of $C_{70}^{\bullet -}$ at 1380 nm seems to be a mirror image of the decay of the absorption of ${}^{T}C_{70}^{*}$.

From these observations, electron transfer takes place *via* ${}^{T}C_{60}^{*}$ and ${}^{T}C_{70}^{*}$ as shown in Scheme 1.

$$C_{60}/C_{70} \xrightarrow[532\ \text{nm}]{h\nu} {}^{S}C_{60}^{*}/{}^{S}C_{70}^{*} \xrightarrow{k_{\text{isc}}}$$

$$ {}^{T}C_{60}^{*}/{}^{T}C_{70}^{*} \xrightarrow[k_{\text{et}}^{T}]{+\ \text{TEOE}} C_{60}^{\bullet -}/C_{70}^{\bullet -} + \text{TEOE}^{\bullet +}$$

Scheme 1

Immediately after the laser pulse, C_{60} and C_{70} are excited to their lowest excited singlet states ${}^{S}C_{60}^{*}$ and ${}^{S}C_{70}^{*}$, which are converted into ${}^{T}C_{60}^{*}$ and ${}^{T}C_{70}^{*}$ with the rate of *ca.* 10^{9} s^{-1} in high quantum yields of 0.99 and 0.97, respectively.[26,34–37] Then, ${}^{T}C_{60}^{*}$ and ${}^{T}C_{70}^{*}$ abstract an electron from TEOE having high electron donor ability [oxidation potential (E_{ox}) is 0.32 V *vs.* standard calomel electrode (SCE) and ionization potential is less than 7.2 eV].[16]

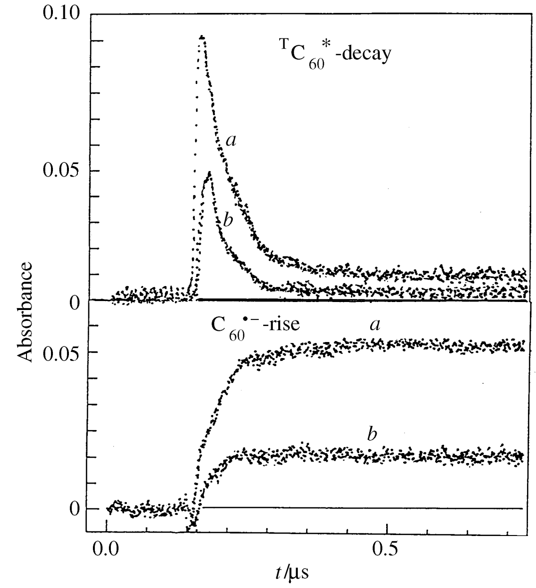

Fig. 4 O_2-effect on time profiles for ${}^{T}C_{60}^{*}$-decay and $C_{60}^{\bullet -}$-rise: (*a*) in Ar-saturated (2.5×10^{-4} mol dm^{-3} of C_{60} and 1.0×10^{-2} mol dm^{-3} of TEOE) and (*b*) in O_2-saturated solution

The free-energy changes (ΔG_{o}) are calculated from the Rehm–Weller equations to be $\Delta G_{o} = -73.3$ kJ mol^{-1} for ${}^{T}C_{60}^{*}$–TEOE and $\Delta G_{o} = -78.2$ kJ mol^{-1} for ${}^{T}C_{70}^{*}$–TEOE by employing the lowest triplet energies ($T_1 = 1.53$ eV for ${}^{T}C_{60}^{*}$ and $T_1 = 1.50$ eV for ${}^{T}C_{70}^{*}$),[38] reduction potentials ($E_{red} = -0.51$ eV for C_{60} and $E_{red} = -0.43$ eV for C_{70}),[39–43] $E_{ox} = 0.32$ eV for TEOE[16] and Coulombic energy of 0.06 eV in benzonitrile.[10] These negative ΔG_{o} values allow fast electron transfer reactions for both ${}^{T}C_{60}^{*}$–TEOE and ${}^{T}C_{70}^{*}$–TEOE; ${}^{T}C_{70}^{*}$ is a slightly stronger electron acceptor than ${}^{T}C_{60}^{*}$.

In order to confirm the electron transfer *via* ${}^{T}C_{60}^{*}$, O_2 was added to the solution of C_{60}–TEOE. Fig. 4 shows the rise curves of $C_{60}^{\bullet -}$ in deoxygenated solution and in O_2-saturated solution. On addition of O_2, $C_{60}^{\bullet -}$ formation was partially suppressed. The decay of ${}^{T}C_{60}^{*}$ was accelerated on addition of O_2 to ${}^{T}C_{60}$–TEOE solution, indicating that energy transfer from ${}^{T}C_{60}^{*}$ to O_2 takes place in addition to the electron transfer reaction between ${}^{T}C_{60}^{*}$ and TEOE. Both reactions may be competitive; *i.e.* the rate constant (k_{O_2}) for the energy transfer from ${}^{T}C_{60}^{*}$ to O_2 was reported to be *ca.* 10^{9} dm^{3} mol^{-1} s^{-1}.[30] If $k_{O_2}[O_2] \gg k_{et}^{T}[\text{TEOE}]$, $C_{60}^{\bullet -}$ formation may be completely suppressed. Our finding that 30% of $C_{60}^{\bullet -}$ was remaining in the O_2-saturated solution suggests that $k_{O_2}[O_2] : k_{et}^{T}[\text{TEOE}] = 1:3$.

On the other hand, if electron transfer takes place *via* ${}^{S}C_{60}^{*}$ from TEOE (k_{et}^{S}), appreciable amounts of $C_{60}^{\bullet -}$ can be observed. In this case, $k_{et}^{S}[\text{TEOE}]$ may be competitive with k_{isc} (*ca.* 10^{9} s^{-1});[26,36] since $[\text{TEOE}] = 10^{-2}$ mol dm^{-3}, k_{et}^{S} should be *ca.* 10^{11} dm^{3} mol^{-1} s^{-1}, which is far greater than the diffusion-controlled limit in benzonitrile (*ca.* 5.6×10^{9} mol^{-1} dm^{3} s^{-1}).[44] Thus, the contribution of ${}^{S}C_{60}^{*}$ route to the $C_{60}^{\bullet -}$ formation is implausible.

Rate constants and quantum yields

Decay curves of ${}^{T}C_{70}^{*}$ are shown in Fig. 5. Each decay curve obeys first-order kinetics giving a linear relationship between ln(Abs) and time. The slope yields the first-order rate constants (k_{1st}^{obs}), which increase with [TEOE]. The pseudo-first-order plot gives the quenching rate constant (k_{qT}^{obs}) for ${}^{T}C_{70}^{*}$ with TEOE (1.3×10^{9} dm^{3} mol^{-1} s^{-1} in benzonitrile). For ${}^{T}C_{60}^{*}$ with TEOE, k_{qT}^{obs} value was similarly obtained as listed in Table 1.

Table 1 Rate constants for ${}^{T}C_{60}^{*}/{}^{T}C_{70}^{*}$-quenching ($k_{qT}^{obs}$) and $C_{60}^{\bullet -}/C_{70}^{\bullet -}$ formation ($k_{C_{60}^{\bullet -}}^{obs}/k_{C_{70}^{\bullet -}}^{obs}$), quantum yield ($\Phi_{et}^{T}$) and k_{et}^{T} for TEOE in benzonitrile, benzene and their mixtures

	C_{60}				C_{70}			
Solvent[a]	k_{qT}^{obs}/ dm^3 mol^{-1} s^{-1}	$k_{C_{60}^{\bullet -}}^{obs}$/ dm^3 mol^{-1} s^{-1}	Φ_{et}^{T}	k_{et}^{T}/ dm^3 mol^{-1} s^{-1}	k_{qT}^{obs}/ dm^3 mol^{-1} s^{-1}	$k_{C_{70}^{\bullet -}}^{obs}$/ dm^3 mol^{-1} s^{-1}	Φ_{et}^{T}	k_{et}^{T}/ dm^3 mol^{-1} s^{-1}
BN	1.4×10^9	1.5×10^9	0.80[b]	1.1×10^9	1.3×10^9	(1.2×10^9)	1.10[c]	1.3×10^9
2:1	1.9×10^9	1.6×10^9	0.64[b]	1.3×10^9	7.1×10^8	(1.1×10^9)	0.88[c]	6.2×10^8
1:1	2.2×10^9	1.9×10^{10}	0.41[b]	9.1×10^8	9.7×10^8	(1.0×10^9)	0.45[c]	4.3×10^8
BZ	2.0×10^9	—	0.26[b]	5.2×10^8	4.2×10^9	—	0.17[c]	7.1×10^8

[a] BN; benzonitrile, BZ; benzene, 2:1 and 1:1; mixture of BN and BZ. [b] $\varepsilon_{C_{60}^{\bullet -}} = 12\,000$ dm^3 mol^{-1} cm^{-1} at 1070 nm[46] and $\varepsilon_{C_{70}^{\bullet -}} = 4000$ dm^3 mol^{-1} cm^{-1} at 1380 nm;[12] $\varepsilon_{{}^{T}C_{60}^{*}} = 16\,000$ dm^3 mol^{-1} cm^{-1} at 750 nm[47] and $\varepsilon_{{}^{T}C_{70}^{*}} = 6000$ dm^3 mol^{-1} cm^{-1} at 980 nm.[45] [c] $C_{60}^{\bullet -}$ and $C_{70}^{\bullet -}$ show fast decay in benzene.

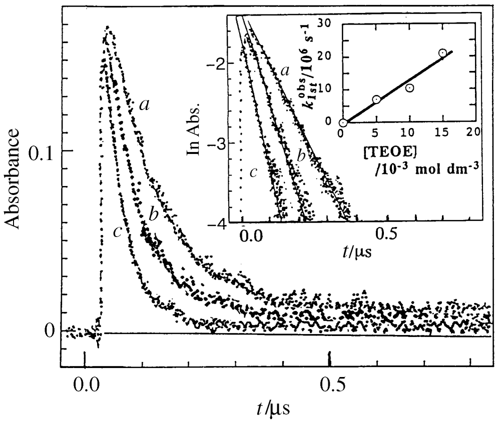

Fig. 5 TEOE-concentration effect on ${}^{T}C_{70}^{*}$-decay time profile; [TEOE] (*a*) 5.0×10^{-3}, (*b*) 1.0×10^{-2} and (*c*) 1.5×10^{-2} mol dm^{-3}. Insert: pseudo-first order plot.

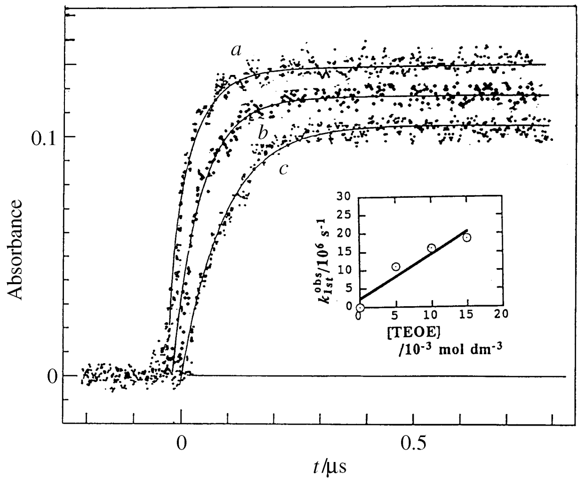

Fig. 6 TEOE-concentration effect on $C_{70}^{\bullet -}$-rise time profile; [TEOE] (*a*) 5.0×10^{-3}, (*b*) 1.0×10^{-2} and (*c*) 1.5×10^{-2} mol dm^{-3}. Insert: pseudo-first order plot.

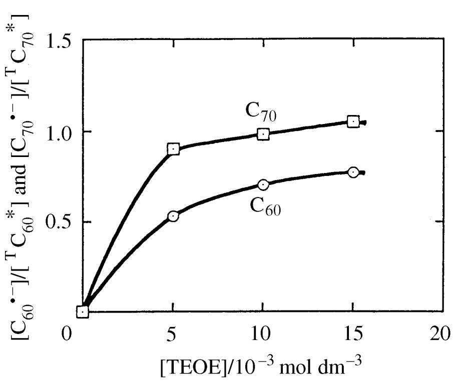

Fig. 7 $[C_{60}^{\bullet -}]/[{}^{T}C_{60}^{*}]$ and $[C_{70}^{\bullet -}]/[{}^{T}C_{70}^{*}]$ *vs.* [TEOE] in benzonitrile

The rise curves of $C_{70}^{\bullet -}$ in benzonitrile are shown in Fig. 6. By the curve-fitting method, the first-order rate constants are evaluated. By the pseudo-first-order plot, the rate constant ($k_{C_{70}^{\bullet -}}^{obs}$) for $C_{70}^{\bullet -}$ formation was evaluated to be 1.2×10^9 dm^3 mol^{-1} s^{-1}, which is in good agreement with k_{qT}^{obs} (1.3×10^9 dm^3 mol^{-1} s^{-1}) as the general relation $k_{qT}^{obs} = k_{C_{70}^{\bullet -}}^{obs}$ predicts.[45]

In Table 1, k_{qT}^{obs} (or $k_{C_{60}^{\bullet -}}^{obs}$) for C_{60} tends to increase with decreasing the solvent polarity. In the case of C_{70}, k_{qT}^{obs} (or $k_{C_{70}^{\bullet -}}^{obs}$) does not strongly depend on the solvent polarity, except in benzene. In order to clarify these solvent polarity changes in the observed rate constants, the quantum yield (Φ_{et}^{T}) for electron transfer *via* the triplet state was evaluated as follows: $[C_{60}^{\bullet -}]/[{}^{T}C_{60}^{*}]$ and $[C_{70}^{\bullet -}]/[{}^{T}C_{70}^{*}]$ were evaluated on substituting the reported molar extinction coefficients for these species.[2,12,46,47] For $[C_{60}^{\bullet -}]/[{}^{T}C_{60}^{*}]$ and $[C_{70}^{\bullet -}]/[{}^{T}C_{70}^{*}]$, the maximal values are adopted; *i.e.* $[{}^{T}C_{60}^{*}]$ and $[{}^{T}C_{70}^{*}]$ are calculated from the initial absorbance, while $[C_{60}^{\bullet -}]$ and $[C_{70}^{\bullet -}]$ are calculated from the maximal absorbance. These $[C_{60}^{\bullet -}]/[{}^{T}C_{60}^{*}]$ and $[C_{70}^{\bullet -}]/[{}^{T}C_{70}^{*}]$ values are plotted against [TEOE] as shown in Fig. 7. Both curves show the saturation, yielding Φ_{et}^{T}.[48] $\Phi_{et}^{T} = 0.8$ for C_{60} and $\Phi_{et}^{T} = 1.1$ for C_{70} in benzonitrile were evaluated. The Φ_{et}^{T} for C_{70} is slightly more than unity, which is likely to come from the uncertainty of ε values of these transient species (the ε values used in this study are cited in Table 1). For each fullerene, Φ_{et}^{T} values decrease with decreasing the solvent polarity (Table 1). The Φ_{et}^{T} for C_{70} is greater than that for C_{60}, excepting those in benzene. On the other hand, $(1 - \Phi_{et}^{T})$, which can be attributed to collisional quenching of ${}^{T}C_{60}^{*}$ by TEOE, increases with decreasing solvent polarity. Even in benzonitrile, $(1 - \Phi_{et}^{T})$ for C_{60} is estimated to be 0.20, indicating that collisional quenching takes place competitively with electron transfer.

The true rate constant for electron transfer *via* the triplet states (k_{et}^{T}) can be evaluated from the relation $k_{et}^{T} = \Phi_{et}^{T}\, k_{qT}^{obs}$ or $k_{et}^{T} = \Phi_{et}^{T}\, k_{C_{60}^{\bullet -}}^{obs}$ (or $k_{et}^{T} = \Phi_{et}^{T}\, k_{C_{70}^{\bullet -}}^{obs}$).[48] They are also listed in Table 1. For each fullerene, the k_{et}^{T} values tend to decrease with decreasing the solvent polarity, although there are exceptions. For C_{60}, the variation of k_{et}^{T} values is small except for that in benzene. On the other hand, the k_{et}^{T} value in benzene is larger than those in benzonitrile–benzene mixtures. In benzonitrile and in benzene, the k_{et}^{T} values for C_{70} are greater than those for C_{60}. In the solvent mixture, on the other hand, the opposite tendency is observed. The k_{et}^{T} values in these solvents may be determined by many factors, such as E_{ox}, E_{red}, Coulombic energy and ε values of $C_{60}^{\bullet -}/C_{70}^{\bullet -}$, which are capable of varying with solvent polarity.

When benzene was used as nonpolar reaction medium, the decay rate of ${}^{T}C_{60}^{*}$ was slightly increased compared with the decay rates in benzonitrile (Fig. 8), suggesting that the quenching of ${}^{T}C_{60}^{*}$ with TEOE takes place more efficiently in nonpolar solvents than polar solvents. In the inserted rise curve of $C_{60}^{\bullet -}$ in Fig. 8, the rise and decay curve in benzene is quite different from those in benzonitrile and in benzonitrile–benzene

Table 2 Back electron transfer rate constats in benzonitrile, benzene and their mixtures

	C_{60}		C_{70}	
Solvent	$(k_{bet}^{2nd}/\varepsilon_{C_{60}^{\bullet -}})$/ $dm^3\ mol^{-1}$	k_{bet}^{2nd}/ $dm^3\ mol^{-1}\ s^{-1}$	$(k_{bet}^{2nd}/\varepsilon_{C_{70}^{\bullet -}})$/ $dm^3\ mol^{-1}$	k_{bet}^{2nd}/ $dm^3\ mol^{-1}\ s^{-1}$
BN	1.1×10^6	1.3×10^{10}	1.2×10^6	4.8×10^9
2:1	1.6×10^6	1.9×10^{10}	3.5×10^6	1.4×10^{10}
1:1	2.1×10^6	2.5×10^{10}	4.0×10^6	1.6×10^{10}
BZ		$(k_{bet}^{1st} = 2.6 \times 10^7\ s^{-1})$		(—)[a]

[a] Too small to observe.

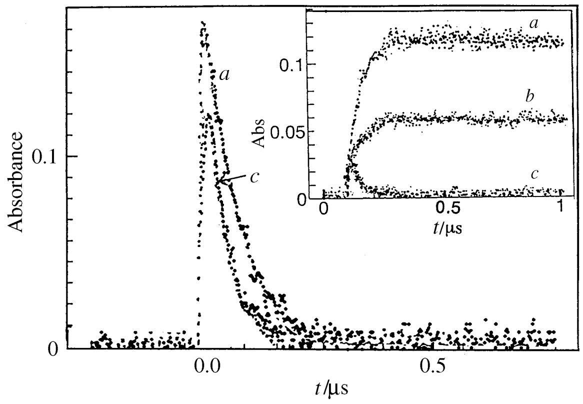

Fig. 8 Solvent polarity effect on time profiles of $^{T}C_{60}$*-decay and $C_{60}^{\bullet -}$-rise in (*a*) benzonitrile and (*b*) benzonitrile–benzene (2:1) and (*c*) benzene

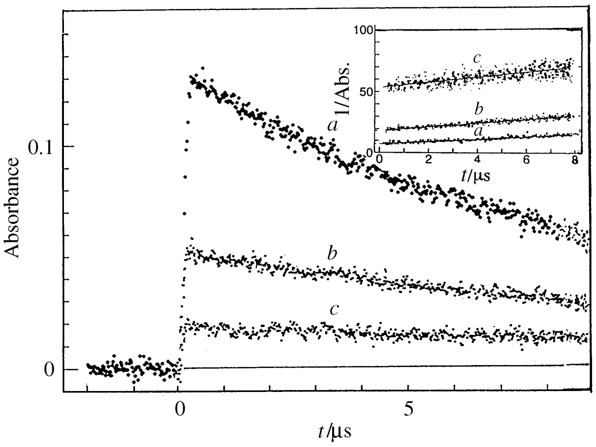

Fig. 9 Solvent polarity effect on decay time profiles of $C_{60}^{\bullet -}$ in (*a*) benzonitrile and (*b*) benzonitrile–benzene (2:1) and (*c*) benzonitrile–benzene (1:1). Insert: second-order plots.

(2:1) mixture. The fast decay of $C_{60}^{\bullet -}$ indicates that the contact ion pair is formed between $C_{60}^{\bullet -}$ and $TEOE^{\bullet +}$ immediately after the nanosecond laser pulse followed by the rapid return the electron from $C_{60}^{\bullet -}$ to $TEOE^{\bullet +}$.

Back electron transfer

After reaching maximal concentration, $C_{60}^{\bullet -}$ begins to decay as shown in Fig. 9, which is illustrated in the long time scale up to 10 μs. The decay of $C_{60}^{\bullet -}$ obeys second-order kinetics in polar benzonitrile and benzonitrile–benzene mixture as shown in inserted plots (k_{bet}^{2nd}). In benzene, on the other hand, the decay of $C_{60}^{\bullet -}$ is very fast as shown in insert to Fig. 8; the decay obeys first-order kinetics (k_{bet}^{1st}). The second-order kinetics indicate that $C_{60}^{\bullet -}$ and $TEOE^{\bullet +}$ recombine after being solvated as free ions or solvent-separated ion pairs, while the first-order kinetic behaviour in benzene arises because of the electron return within the ion pair.[21,22] The slope of the second-order plot yields $k_{bet}^{2nd}/\varepsilon_{C_{60}^{\bullet -}}$ (or $k_{bet}^{2nd}/\varepsilon_{C_{70}^{\bullet -}}$). On substituting $\varepsilon_{C_{60}^{\bullet -}}$ = 12 000 $dm^3\ mol^{-1}\ cm^{-1}$ (or $\varepsilon_{C_{70}^{\bullet -}}$ = 4000 $dm^3\ mol^{-1}\ cm^{-1}$),[12,46] the k_{bet}^{2nd} values are obtained, which are listed in Table 2 with the observed k_{bet}^{1st}. On assuming that $\varepsilon_{C_{60}^{\bullet -}}$ and $\varepsilon_{C_{70}^{\bullet -}}$ did not change much with changing solvent polarity, our observation indicates that the k_{bet}^{2nd} increases slightly with a decrease in the solvent polarity. Finally, in a non-polar solvent, a drastic change was observed as shown in the insert of Fig. 8.

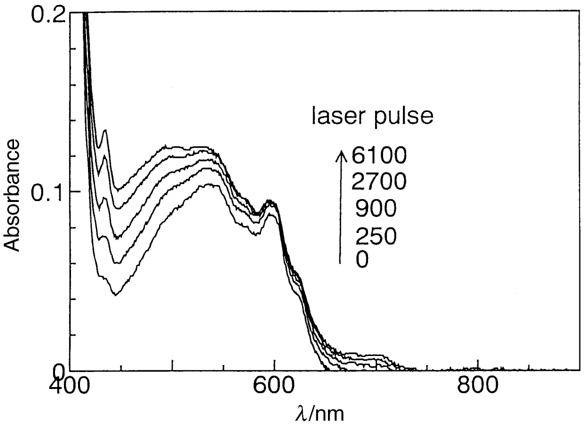

Fig. 10 Change of absorption spectra of mixture of C_{60} (2.5×10^{-4} mol dm^{-3}) and TEOE (1.0×10^{-2} mol dm^{-3}) in benzonitrile by repeated laser pulse irradiation at 532 nm of 7 mJ per pulse

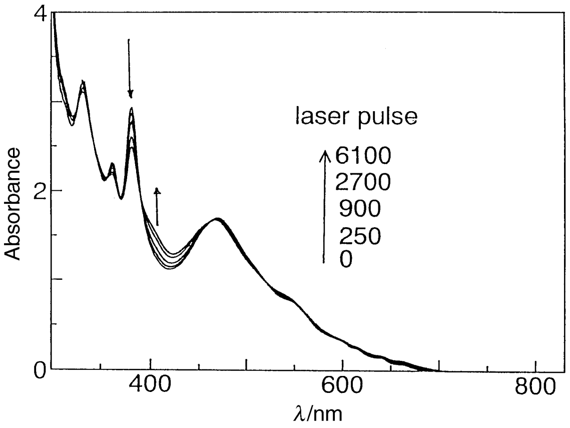

Fig. 11 Change of absorption spectra of mixture of C_{70} (2.5×10^{-4} mol dm^{-3}) and TEOE (1.0×10^{-2} mol dm^{-3}) in benzonitrile by repeated laser pulse irradiation at 532 nm of 7 mJ per pulse

Repeated laser irradiation

After the repeated irradiation of the laser pulses of 532 nm light which predominantly excites C_{60} and C_{70} in benzonitrile, steady UV–VIS spectra were measured as shown in Figs. 10 and 11 for C_{60}–TEOE and C_{70}–TEOE, respectively. In Fig. 10, the absorption peak at 435 nm characteristic of the mono adduct appears with a broad band in the region of 450–550 nm.[10,49] The absorbance change at 435 nm after 6100 laser pulses is 0.08. For C_{70}–TEOE (Fig. 11), the absorption in the region of 390–450 nm was increased by the laser pulse of 532 nm light irradiation with a decrease in the absorbance at 375 nm band due to C_{70}. The structures of the adducts between TEOE and C_{60} or C_{70} were identified by Zhang *et al.* to be those of 1,2-cycloadducts, which are produced thermally.[19,20] They also pointed out that photo-cleavage between C–C of the adducts may take place on irradiation of steady-light onto the adducts. From our spectral changes, it would be anticipated that the adduct may be produced *via* electron transfer *via* $^{T}C_{60}$* or $^{T}C_{70}$* by the irradiation of pulsed laser light at 532 nm in polar solvent. In benzene, on the other hand, any spectral change was not observed under similar conditions, suggesting that back electron transfer rate is fast in addition to the low efficiency of the photoinduced electron transfer in non-polar solvent.

Experimental

C_{60} of 99.99% purity and C_{70} of 99.9% purity were obtained from Texas Fullerenes Corp. Tetraethoxyethene (TEOE) was prepared in the manner described elsewhere.[51,52] The C_{60} (or C_{70}) and TEOE were dissolved in benzonitrile, benzene and their mixture. The solution was deaerated with Ar bubbling before measurements were taken. O_2-saturated solution was made by O_2 bubbling.

The solution was excited by a Nd : YAG laser (Quanta-Ray, GCR-130, 6 ns fwhm) at 532 nm at 7 mJ. A pulsed xenon flash lamp (Tokyo Instruments, XF80–60, 15 J, 60 ms fwhm) was used for the probe beam, which was detected with a Ge-APD module (Hamamatsu, C5331-SPL) after passing through the photochemical quartz vessel (10 mm × 10 mm) and a monochromator.[33] The output from Ge-APD was recorded with a digitizing oscilloscope (HP 54510B, 300 MHz). The steady-state UV–VIS absorption spectra were recorded with a Jasco spectrometer. All experiments were performed at 22 °C.

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