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Electron Transfer from Tetrathiafulvalenes to Photoexcited C_{70} Studied by Observing Transient Absorption in the Near-IR Region

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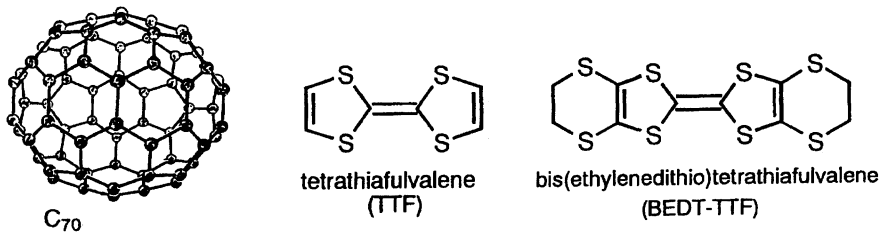
The photoinduced electron transfer between C_{70} and tetrathiafulvalene or bis(ethylenedithio)tetrathiafulvalene in polar and nonpolar solvents and their mixture has been investigated by nanosecond laser photolysis/transient absorption spectroscopy in the visible and near-IR regions. The transient absorption bands of the triplet state of C_{70} observed in polar solvents decayed upon addition of tetrathiafulvalenes accompanied by the appearance of the transient absorption bands of the radical anion of C_{70}. In benzene, the quenching of the triplet state of C_{70} was observed without the appearance of the radical anion of C_{70} within a nanosecond laser pulse, suggesting a collisional quenching of the triplet state of C_{70} with tetrathiafulvalenes. The quantum yield for the formation of the radical anion via the triplet state of C_{70} was about 1 for tetrathiafulvalene in benzonitrile. The quantum yield decreased in less polar solvents. The back electron transfer rates were also evaluated in polar solvents.

The photoinduced electron transfer reactions of fullerenes such as C_{60} and C_{70} have been investigated by various methods, including time-resolved absorption spectroscopy.[1—11] The initial steps of the electron-transfer reactions change depending on the experimental conditions, such as the donor/acceptor abilities, concentration of the donor/acceptor and reaction media. In the presence of electron donors, photoexcited C_{60} and C_{70} act as electron acceptors.[1—9] Under the conditions of low donor concentration in polar solvents, electron transfer takes place via the triplet states of C_{60} and C_{70} (${}^{T}C_{60}^{*}$ and ${}^{T}C_{70}^{*}$).[2,6] The ion radicals are further long-lived up to ca. 50 μs.[1]

Since it was found that the electron conductivity of C_{70} is higher than that of C_{60}, some applications of C_{70} to photoelectronic materials have been investigated.[12,13] Thus, although the importance of research on the photoinduced electron transfer of C_{70} has recently increased, a lower abundance of C_{70} in soot has been found compared with that of C_{60}. In a polar solution, the relation between the electron-transfer rates and the oxidation potentials of the donor molecules has been investigated in order to confirm the Rehm–Weller relation.[6] For these investigations, the quenching rate constants of ${}^{T}C_{70}^{*}$ (k_{qT}^{obs}) were assumed to be equal to the electron-transfer rate constants (k_{et}^{T}), which implies that the quantum yield (Φ_{et}^{T}) of electron-transfer via ${}^{T}C_{70}^{*}$ is unity. It is difficult to evaluate Φ_{et}^{T}, because it is necessary to observe both the transient absorption bands of the radical anion of C_{70} ($C_{70}^{-\bullet}$) and ${}^{T}C_{70}^{*}$ in the near-IR region. In this study, we employed nanosecond laser photolysis with a detector capable of measuring the absorption changes in the near-IR region.

As electron-donors, tetrathiafulvalene (TTF), and bis(ethylenedithio)tetrathiafulvalene (BEDT–TTF) were used in this study (Scheme 1), since these sulfur compounds are known to be good electron donors, forming charge-transfer complexes (or radical ion salts) with various, electron acceptors.[14—19] It has been reported that BEDT–TTF forms a stable radical ion salt with C_{60}.[20] The heterojunction of C_{60}/TTF exhibited a photocurrent.[21] In our previous paper,[22] a photoinduced electron transfer was reported for the systems of C_{60}/TTF's in a dilute solution. In this study we investigated C_{70}/TTF's, and found a higher electron-transfer efficiency for C_{70}/TTF than that for C_{60}/TTF. We also examined the solvent polarity affects on the photo-induced electron-transfer efficiency. Information concerning the back electron transfer rates, which were also solvent dependent, was also obtained.



Scheme 1.

Experimental

C_{70} was obtained from Texas Fullerenes Corp. at a purity of 99%. Commercially available TTF, BEDT–TTF, and solvents were used; benzonitrile and benzene were of HPLC grade and spectrophotometric grade, respectively. C_{70} and TTF (or BEDT–TTF) were dissolved in benzonitrile, benzene, and their mixture; the sample solutions were deaerated by bubbling with argon gas before measurements. An O_2-saturated solution was produced by O_2-bubbling.

C_{70} was excited by a Nd : YAG laser (6 ns fwhm) at 532 nm with a laser power of 5 mJ/pulse. For a transient-absorption measurement with a nanosecond-time-scale in the near-IR region, a Ge-APD module detector (Hamamatsu) attached to a monochromator was employed, using a pulsed Xe-lamp (15 J/pulse, 60 μs fwhm) as the probe light.[23] The response-time of the Ge-APD detector of this system was less than 5 ns, which was about the same duration as the laser pulse. The output signals from the detectors were recorded with a digitizing oscilloscope and analyzed by a personal computer. All of the experiments were carried out at 23 °C.

The steady-state UV-visible absorption spectra were recorded by a UV/vis spectrophotometer (JASCO V-570).

Results and Discussion

Each steady-state absorption spectrum of C_{70} and TTF in benzonitrile was recorded at between 400 and 800 nm, as shown in Fig. 1A. The absorption spectrum of a mixture of C_{70} and TTF in benzonitrile (Fig. 1B) is a superimposition of the components, suggesting no apparent interaction under the concentration range employed by the laser-photolysis experiments in this study (less than 5×10^{-3} mol dm^{-3}).[24,25] The absorption bands of the components were not appreciably affected by the solvent polarity.[26] Even in benzene, the absorption spectrum of the mixture was a superimposition of components similar to that in benzonitrile. By laser photolysis at 532 nm, C_{70} was solely excited, because of the lack of absorption of TTF at this wavelength. For BEDT–TTF, similar steady absorption spectra were obtained, suggestion no strong interaction with C_{70}.

The laser-flash photolysis of C_{70} (0.1×10^{-3} mol dm^{-3}) was carried out in the presence of TTF (1.0—6.0×10^{-3} mol dm^{-3}) in benzene. Figure 2 shows the transient absorption spectra in the visible and near-IR regions. A sharp absorption peak at 980 nm with a small peak at 700 nm, which were observed immediately after the nanosecond laser pulse, are attributed to ${}^{\mathrm{T}}C_{70}^{*}$.[26—29] The initial concentration of ${}^{\mathrm{T}}C_{70}^{*}$ was calculated from the initial absorbance (A_{T}) on the basis of the reported extinction coefficient ($\varepsilon_{\mathrm{T}}=6500$ mol dm^{-3} cm^{-1} at 980 nm)[5,28,29] to be about 2.1×10^{-5} mol dm^{-3}. The decay rate of ${}^{\mathrm{T}}C_{70}^{*}$ increased with [TTF] without the appearance of a new absorption band due to $C_{70}^{-\bullet}$, which would be expected to appear at 1380 nm based on the literature.[30—35] The decay curve of ${}^{\mathrm{T}}C_{70}^{*}$ at 980 nm is shown in the inserted time profiles in Fig. 2. This implies that ${}^{\mathrm{T}}C_{70}^{*}$ was quenched by TTF by processes other than electron transfer. A triplet energy transfer from ${}^{\mathrm{T}}C_{70}^{*}$ to TTF is also implausible because of the low triplet energy of ${}^{\mathrm{T}}C_{70}^{*}$. A collisional deactivation of ${}^{\mathrm{T}}C_{70}^{*}$ with TTF may take place via a weak interaction in the excited state. The decay profile obeys first-order kinetics, from which the quenching rate constant ($k_{\mathrm{c}}^{\mathrm{T}}$) was evaluated, as listed in Table 1. The $k_{\mathrm{c}}^{\mathrm{T}}$ values are in the order 1.2×10^{10} and 4.2×10^{9} mol^{-1} dm^{3} s^{-1} for TTF and BEDT–TTF, respectively.

In benzonitrile, with the decay of ${}^{\mathrm{T}}C_{70}^{*}$, the absorption band of $C_{70}^{-\bullet}$ appears at 1380 nm (Fig. 3). The decay curve of ${}^{\mathrm{T}}C_{70}^{*}$ at 980 nm and the rise curve of $C_{70}^{-\bullet}$ at 1380 nm are shown in the inserted time profiles in Fig. 3. The decay profile and the rise profile obey first-order kinetics, which implies that 10^{-3} mol dm^{-3} of TTF is a large excess compared with $[{}^{\mathrm{T}}C_{70}^{*}]_{\mathrm{initial}}=2.5\times10^{-5}$ mol dm^{-3}. $C_{70}^{-\bullet}$ begins to decay after reaching a maxima at about 400 ns. The absorption band of $\mathrm{TTF}^{+\bullet}$ would be expected in a shorter wavelength region than 600 nm; thus, no absorption band of $\mathrm{TTF}^{+\bullet}$ appears in the near-IR region.[14] The rise-curves of $C_{70}^{-\bullet}$ in deaerated, aerated and O_2-saturated benzonitrile solutions are shown in Fig. 4. Along with an increase in the O_2 concentration, the yield of $C_{70}^{-\bullet}$ decreases; upon the addition of air, about

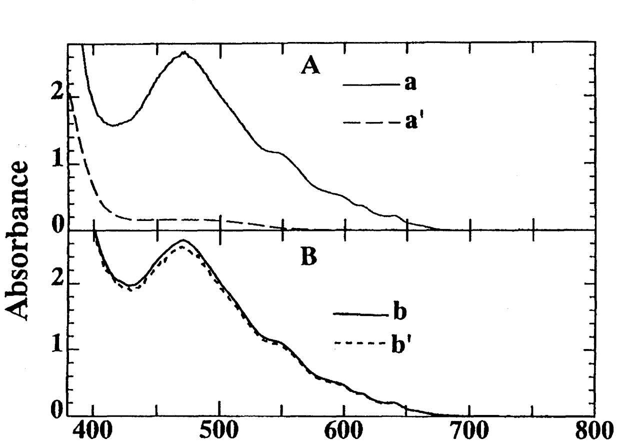


Fig. 1. Steady-state absorption spectra of (a) C_{70} (0.1×10^{-3} mol dm^{-3}), (a′) TTF (1.0×10^{-3} mol dm^{-3}), (b) synthesized spectrum, and (b′) observed spectrum of the mixture of C_{70} and TTF in benzonitrile.

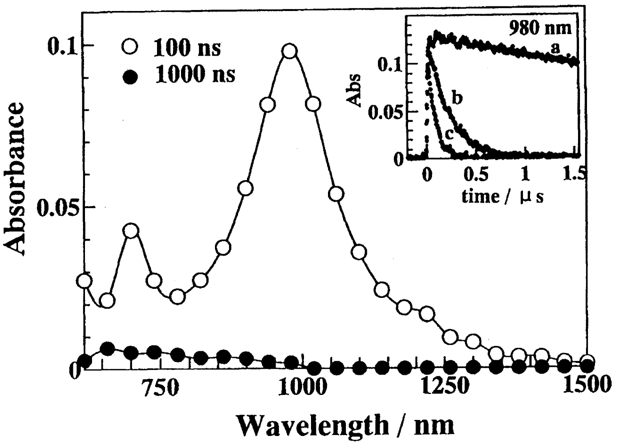


Fig. 2. Transient absorption spectra obtained by 532 nm laser flash photolysis of C_{70} (0.1 mmol dm^{-3}) in the presence of TTF (1.0 mmol dm^{-3}) in deaerated benzene. Insert: Decay profiles of ${}^{\mathrm{T}}C_{70}^{*}$ at 980 with TTF (in 10^{-3} mol dm^{-3}); (a) 0.0, (b) 0.2, and (c) 1.0.

Table 1. $^{T}C_{70}^{*}$-Quenching Rate Constants (k_{qT}^{obs}), Quantum Yield (Φ_{et}^{T}),[a] k_{et}^{T} ($= \Phi_{et}^{T} \times k_{qT}^{obs}$)[b] and k_{c}^{T} [$=(1-\Phi_{et}^{T})k_{qT}^{obs}$] for TTF and BDET–TTF

Solvent	TTF				BEDT-TTF			
	k_{qT}^{obs}	Φ_{et}^{T}	k_{et}^{T}	k_{c}^{T}	k_{qT}^{obs}	Φ_{et}^{T}	k_{et}^{T}	k_{c}^{T}
	mol^{-1} dm^{3} s^{-1}		mol^{-1} dm^{3} s^{-1}	mol^{-1} dm^{3} s^{-1}	mol^{-1} dm^{3} s^{-1}		mol^{-1} dm^{3} s^{-1}	mol^{-1} dm^{3} s^{-1}
BZ	1.2×10^{10}	0	0	1.2×10^{10}	4.2×10^{9}	0	0	4.2×10^{9}
1 : 1	1.8×10^{10}	0.40	7.6×10^{9}	1.0×10^{10}	3.9×10^{10}	0.23	9.0×10^{8}	3.0×10^{9}
BN	5.5×10^{9}	1.00	5.5×10^{9}	0	1.8×10^{9}	0.51	9.2×10^{8}	8.8×10^{8}

a) $[C_{70}^{\bullet-}]_{max}/[^{T}C_{70}^{*}]_{initial}$ was calculated using the observed absorbances and reported ε values; ε of $^{T}C_{70}^{*}$ at 980 nm (6500 mol^{-1} dm^{3} cm^{-1}),5,28,29) ε of $C_{70}^{\bullet-}$ at 1380 nm (4000 mol^{-1} dm^{3} cm^{-1}).32,34) b) Refs. 9 and 22. c) BZ; benzene, BN: benzonitrile, 1 : 1; benzene : benzonitrile (1 : 1).

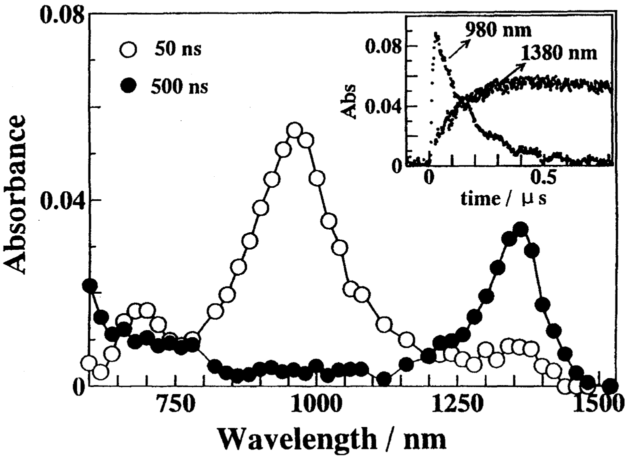


Fig. 3. Transient absorption spectra obtained by 532 nm laser photolysis of C_{70} (0.1×10^{-3} mol dm^{-3}) in the presence of TTF (1.0×10^{-3} mol dm^{-3}) in deaerated benzonitrile. Insert: Time profiles at 980 and 1380 nm.

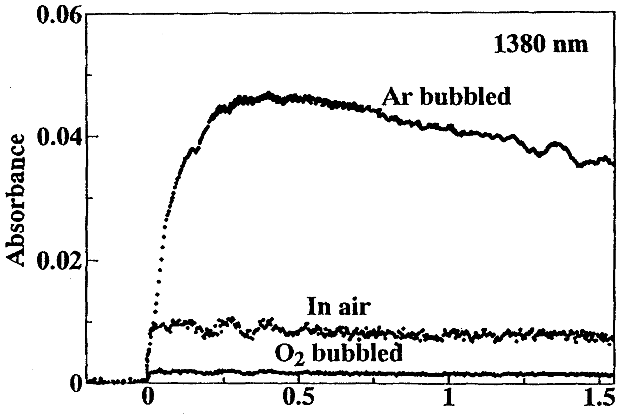
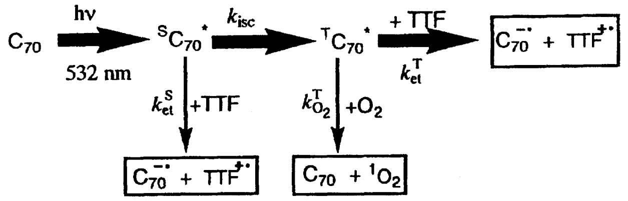


Fig. 4. Rise-curves of $C_{70}^{\bullet-}$ in Ar-saturated, air-saturated and O_2-saturated solutions for TTF (1×10^{-3} mol dm^{-3}).

2/3 of $C_{70}^{\bullet-}$ was decreased and in an O_2-saturated solution, about 90% of $C_{70}^{\bullet-}$ disappeared. This also confirms that $C_{70}^{\bullet-}$ is mainly formed via $^{T}C_{70}^{*}$. About 10% of $C_{70}^{\bullet-}$ may be produced via the excited singlet state of C_{70} ($^{S}C_{70}^{*}$) or via an exciplex route. The observed electron-transfer mechanism for C_{70} is illustrated in Scheme 2.

In an O_2-saturated solution, $k_{O_2}[O_2] > k_{et}^{T}$[TTF] can be assumed, implying that an electron transfer via $^{T}C_{70}^{*}$ is almost inhibited. The observed ratio of $C_{70}^{\bullet-}$ in an O_2-saturated solution to that in a deaerated solution was 0.1 at [TTF] = 10^{-3} mol dm^{-3}, suggesting that the ratio of the electron-transfer rate via $^{S}C_{70}^{*}$ (k_{et}^{S}[TTF]) to k_{isc} is about 0.1. Thus, k_{et}^{S}[TTF] is estimated to 1.2×10^{8} s^{-1} on the basis of $k_{isc} = 1.2\times10^{9}$ s^{-1}.5) Then, k_{et}^{S} is 1.2×10^{11} mol^{-1} dm^{3} s^{-1}, which is about 25-times greater than the diffusion-controlled limit (5.2×10^{9} mol^{-1} dm^{3} s^{-1} in benzonitrile). Even though such a high rate constant exists for k_{et}^{S}, the singlet route is minor compared with the triplet route, because the singlet route must be competitive with the fast intersystem crossing rate.



Scheme 2.

In the case of C_{70} with BEDT–TTF, a similar photoinduced electron-transfer behavior was observed in polar solvents. The rise rate of $C_{70}^{\bullet-}$ at 1380 nm in benzonitrile increases with the concentration of BEDT–TTF, as shown in Fig. 5. The first-order rate constants for the growth of $C_{70}^{\bullet-}$ can

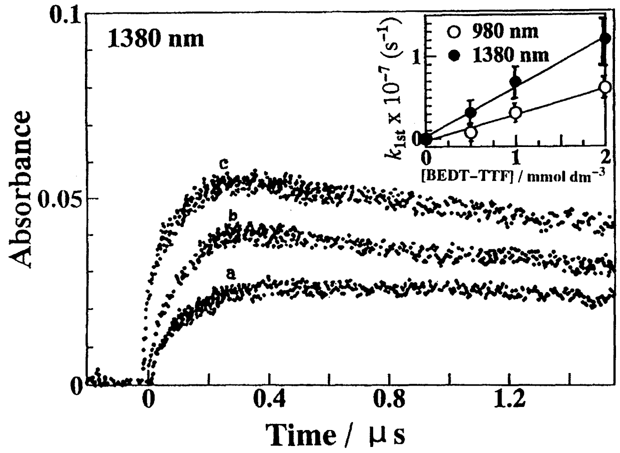
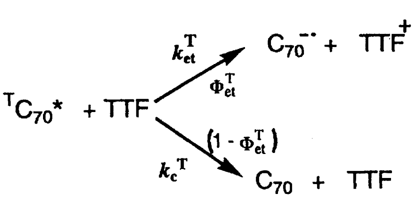


Fig. 5. Rise-curves of $C_{70}^{\bullet-}$ at 1380 nm with BEDT–TTF (in 10^{-3} mol dm^{-3}); (a) 0.5, (b) 1.0, and (c) 2.0 in deaerated benzonitrile. Insert: Pseudo-first-order plots for the rise of $C_{70}^{\bullet-}$ and decay of $^{T}C_{70}^{*}$ at 980 nm.



Scheme 3.

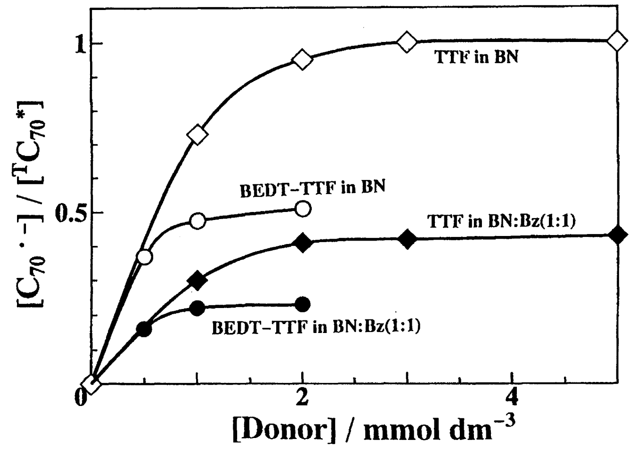


Fig. 6. Dependence of formation efficiency of $C_{70}^{-\bullet}$ via $^TC_{70}^*$ on the concentration of TTF and BEDT–TTF.

be evaluated with a curve-fitting method. The slope of the pseudo-first-order plot (insert in Fig. 5) gives the rate constant for the rise of $C_{70}^{-\bullet}$ (k_A^{obs}). Although $k_{qT}^{obs} = k_A^{obs}$ would be anticipated,[9,19] the k_A^{obs} value seems to be slightly larger than k_{qT}^{obs}. The experimental and estimation errors are greater for k_A^{obs} than those of k_{qT}^{obs}, due to the overlap of the absorption tail of $^TC_{70}^*$ with the absorption maxima of $C_{70}^{-\bullet}$. The observed second-order rate constants (k_{qT}^{obs}) are listed in Table 1 for C_{70} with TTF and BEDT–TTF in benzonitrile.

The Φ_{et}^T was evaluated from the ratio of the maximal $[C_{70}^{-\bullet}]$ to the initial $[^TC_{70}^*]$, since both absorption bands were observed in the near-IR region. Upon substituting the reported extinction coefficients,[9,26,29] the ratio ($[C_{70}^{-\bullet}]_{max}/[^TC_{70}^*]_{init}$) was estimated. In Fig. 6, $[C_{70}^{-\bullet}]_{max}/[^TC_{70}^*]_{init}$ is plotted against [TTF]. The $[C_{70}^{-\bullet}]_{max}/[^TC_{70}^*]_{max}$ increases with [TTF], reaching a plateau, which is defined as the quantum yield (Φ_{et}^T) of the electron transfer of $C_{70}^{-\bullet}$ formation via $^TC_{70}^*$. The Φ_{et}^T values are also summarized in Table 1. The Φ_{et}^T value of C_{70}/TTF in benzonitrile is ca. 1.00, which is greater than that of C_{60}/TTF (0.75 in benzonitrile),[22] indicating that $^TC_{70}^*$

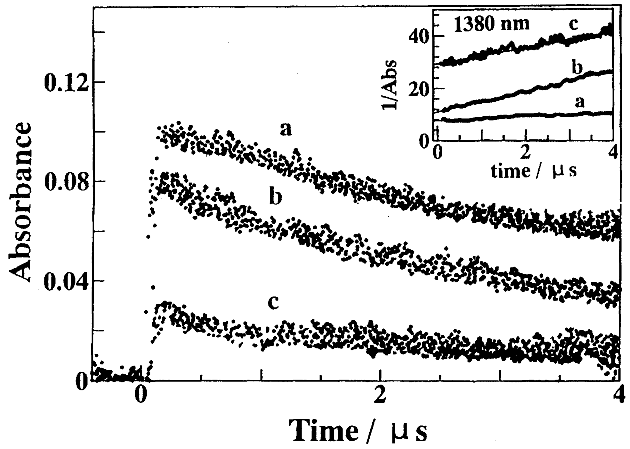


Fig. 7. Rise and decay curves of $C_{70}^{-\bullet}$ at 1380 nm for (a) TTF in benzonitrile, (b) BEDT–TTF in benzonitrile, and (c) BEDT–TTF in benzonitrile : benzene (1 : 1) mixture. Insert: Second-order plots for decays of $C_{70}^{-\bullet}$ at 1380 nm.

$$C_{70}^{-\bullet} + TTF^{+\bullet} \xrightarrow{k_{bet}} C_{70} + TTF$$

Scheme 4.

has a higher electron affinity than that of $^TC_{60}^*$. The Φ_{et}^T value of C_{70}/BEDT–TTF (0.51 in benzonitrile) is about half of that of C_{70}/TTF in benzonitrile. The Φ_{et}^T in benzene is zero, suggesting collisional quenching.

For C_{70}/TTF in a 1 : 1 mixture of benzonitrile : benzene, the absorption band of $C_{70}^{-\bullet}$ appears at 1380 nm with the decay of the absorption band of $^TC_{70}^*$ at 980 nm. The decay rate of $^TC_{70}^*$ at 980 nm in a 1 : 1 mixture solution is faster than that of in benzonitrile (Table 1), as is the fast rise of $C_{70}^{-\bullet}$ at 1380 nm. In general, it would be anticipated that less polar solvents retard the electron transfer.[34] However, the observed tendency for k_{qT}^{obs} in Table 1 is opposite. This suggests that k_{qT}^{obs} is the apparent value, including the collisional deactivation of $^TC_{70}^*$ by TTF's. In order to evaluate the real electron-transfer rate constant (k_{et}^T), it is necessary to multiply Φ_{et}^T by k_{qT}^{obs} (Scheme 3).[9]

In Table 1, the Φ_{et}^T values in a benzonitrile : benzene (1 : 1) mixture decrease until about a half of the corresponding value in benzonitrile, indicating that the electron transfer is competitive with the collisional quenching. This is reasonably interpreted by the stabilization of the ion radicals in a polar solvent.[36] Then, the k_{et}^T value for C_{70}/BEDT–TTF

Table 2. Rate Constants of Back Electron Transfer (k_{bet}) from $C_{70}^{-\bullet}$ to $TTF^{+\bullet}$ and BEDT–$TTF^{+\bullet}$

Solvent[a)]	TTF		BEDT–TTF	
	k_{bet}/ε_A / cm s^{-1}	k_{bet} / mol^{-1} dm^3 s^{-1}	k_{bet}/ε_A / cm s^{-1}	k_{bet} / mol^{-1} dm^3 s^{-1}
BZ	—[c)]	—[c)]	—[c)]	—c)
1 : 1	3.3×10^6	1.3×10^{10}	3.1×10^6	1.2×10^{10}
BN	7.6×10^5	3.0×10^9	4.7×10^5	1.9×10^9

a) BN; benzonitrile, BZ; benzene, and 1 : 1; mixture of BN and BZ. b) $\varepsilon_A = 4000$ mol^{-1} dm^3 cm^{-1} (Refs. 32 and 34). c) $C_{70}^{-\bullet}$ was not observed in benzene.

becomes almost the same as that in benzonitrile (Table 1). For C_{70}/TTF, the $k_{\rm et}^{\rm T}$ value is still slightly larger than that in benzonitrile.

From the Rehm–Weller equation,37) the free-energy change ($\Delta G_{\rm o}$) can be calculated to be -75.3 kJ mol^{-1} for C_{70}/TTF and -58.7 kJ mol^{-1} for C_{70}/BEDT–TTF in benzonitrile by employing the T_1-energy level of $^{\rm T}C_{70}^{*}$ (1.50 eV),38) the reduction potential of C_{70} (-0.43 eV),20,39,40) the oxidation potentials of the electron-donors (0.35 eV for TTF and 0.54 eV for BEDT–TTF)14,16,18) and the Coulomb energy (0.06 eV).6) These negative $\Delta G_{\rm o}$ values anticipate that the $k_{\rm et}^{\rm T}$ value is as large as the diffusion-controlled limit (5.2×10^9 mol^{-1} dm^3 s^{-1} in benzonitrile). The $k_{\rm c}^{\rm T}$ value, which can be calculated by $(1-\Phi_{\rm et}^{\rm T})\times k_{\rm qT}^{\rm obs}$, is greater in benzene than that in benzonitrile, because of the lower viscosity of benzene. The $\Delta G_{\rm o}$ value for C_{70}/TTF is slightly more negative than that for C_{60}/TTF (-70.45 kJ mol^{-1}),22) which is in accord with the observed high $\Phi_{\rm et}^{\rm T}$ and $k_{\rm et}^{\rm T}$. The $\Delta G_{\rm o}$ value for C_{70}/TTF is more negative than that for C_{70}/BEDT–TTF, which is also in accord with the observed high $\Phi_{\rm et}^{\rm T}$ and large $k_{\rm et}^{\rm T}$; such a large difference may come from the difference in the oxidation potentials.

In benzene, the reason why $C_{70}^{-\bullet}$ was not observed with our nanosecond-laser photolysis, can be explained by two possible considerations. The first one is that the electron transfer takes place within a nano-second, forming a contact ion pair which quickly returns to neutral molecules. In this case, the electron transfer occurs without via $^{\rm T}C_{70}^{*}$. The second one is that the electron transfer does not take place at all. The latter is more plausible, because of the lack of a strong charge-transfer interaction, the low concentration of the electron donor employed in this study, and the observed large $k_{\rm c}^{\rm T}$ values.

After reaching a maximum, $C_{70}^{-\bullet}$ begins to decay, as shown in Fig. 7. The second-order plots show a linear line, indicating that a back electron transfer reaction ($k_{\rm bet}$) takes place (Scheme 4). From the slopes of the second-order plots, the ratio of $k_{\rm bet}$ to the molar extinction coefficient of $C_{70}^{-\bullet}$ ($k_{\rm bet}/\varepsilon_{\rm A}$) can be obtained. Upon substituting $\varepsilon_{\rm A}$ (4,000 mol^{-1} dm^3 at 1380 nm in benzonitrile),32,34) the $k_{\rm bet}$ values are evaluated as summarized in Table 2. When 50% benzene was added to benzonitrile, the $k_{\rm bet}$ values increase about 2 or 3 times, assuming the same ε value for $C_{70}^{-\bullet}$ to that in benzonitrile. With decreasing the solvent polarity, the $k_{\rm bet}$ values tend to increase, suggesting that ion radicals in a less polar solvent exist as a kind of ion pairs.

The steady state absorption spectra did not change at all by repeated exposure to 532 nm-laser light for C_{70}/TTF until 10000 shots at a laser power of 10 mJ. Thus, this system is photochemically very stable.

Summary

By directly observing the rise of $C_{70}^{-\bullet}$ in addition to the decay of $^{\rm T}C_{70}^{*}$ at the same time, an electron transfer via $^{\rm T}C_{70}^{*}$ was confirmed in polar solvents, which was also supported by the decrease of $C_{70}^{-\bullet}$ upon the addition of O_2. The electron-transfer rates were evaluated by combining the observed quantum yield and the decay rate of $^{\rm T}C_{70}^{*}$ (or rise of $C_{70}^{-\bullet}$). In benzene, collisional quenching takes place without $C_{70}^{-\bullet}$ formation. The solvent polarity dependence of the back electron-transfer rates was also revealed.

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References

1) J. W. Arbogast and C. S. Foote, *J. Am. Chem. Soc.*, **113**, 8886 (1991).

2) J. W. Arbogast, C. S. Foote, and M. Kao, *J. Am. Chem. Soc.*, **114**, 2277 (1992).

3) K. C. Hwang and D. Mauzerall, *J. Am. Chem. Soc.*, **114**, 9705 (1992).

4) D. K. Palit, A. V. Sapre, J. P. Mittal, and C. N. R. Rao, *Chem. Phys. Lett.*, **195**, 1 (1992).

5) R. M. Fraelich and R. B. Weisman, *J. Phys. Chem.*, **97**, 11145 (1993).

6) T. Osaki, Y. Tai, M. Tazawa, S. Tanemura, K. Inukawa, K. Ishiguro, Y. Sawaki, Y. Saito, H. Shinohara, and H. Nagashima, *Chem. Lett.*, **1993**, 789.

7) J. Park, D. Kim, Y. D. Suh, and S. K. Kim, *J. Phys. Chem.*, **98**, 8722 (1994).

8) A. Watanabe and O. Ito, *Jpn. J. Appl. Phys.*, **34**, 194 (1995).

9) C. A. Steren, H. van Willigen, L. Biczok, N. Gupta, and H. Linschitz, *J. Phys. Chem.*, **100**, 8920 (1996).

10) C. A. Steren, P. R. levstein, H. van Willigen, H. Linschitz, and L. Biczok, *Chem. Phys. Lett.*, **204**, 23 (1993).

11) S. Michaeli, V. Meiklyar, M. Schulz, K. Mobius, and H. L. Levanon, *J. Phys. Chem.*, **98**, 7444 (1994).

12) M. Hosoya, K. Ichimura, Z. H. Wang, G. Dresselhaus, and M. S. Dresselhaus, *Phys. Rev. B*, **49**, 4981 (1994).

13) A. Hirao, H. Nishizawa, H. Miyamoto, M. Sugiuchi, and M. Hosoya, *SPIE*, **2526**, 71 (1995).

14) S. Hunig, G. Kiesslich, H. Quast, and D. Scheutzow, *Liebigs Ann. Chem.*, **766**, 310 (1973).

15) K. Nakasuji, M. Nakatsuka, H. Yamochi, I. Murata, S. Harada, N. Kasai, K. Yamamura, J. Tanaka, G. Saito, T. Enoki, and H. Inokuchi, *Bull. Chem. Soc. Jpn.*, **59**, 207 (1986).

16) W. Chen, M. P. Cava, M. A. Takassi, and R. M. Metzger, *J. Am. Chem. Soc.*, **110**, 7903 (1988).

17) D. L. Lichtenberger, R. L. Johnston, K. Hinkelmann, T. Suzuki, and F. Wudl, *J. Am. Chem. Soc.*, **112**, 3302 (1990).

18) G. Grampp, A. Kapturkiewicz, and W. Jaenicke, *Ber. Bunsenges. Phys. Chem.*, **94**, 439 (1990).

19) M. R. Bryce, *Chem. Rev.*, **20**, 355 (1991).

20) A. Izuoka, T. Tachikawa, T. Sugawara, Y. Suzuki, M. Konno, Y. Saito, and H. Shinohara, *J. Chem. Soc., Chem. Commun.*, **1992**, 1472.

21) Y. Yamashita, W. Takashima, and K. Kaneto, *Jpn. J. Appl. Phys.*, **32**, L1017 (1993).

22) M. M. Alam, A. Watanabe, and O. Ito, *J. Photochem. Photobiol. A*, **104**, 59 (1997).

23) A. Watanabe and O. Ito, *J. Phys. Chem.*, **98**, 7736 (1994).

24) H. Ajie, M. M. Alvarez, S. J. Anz, R. D. Beck, F. Diederich, K. Fostiropoulos, D. R. Hiffman, W. Kratschmer, Y. Rubin, K. E. Schriver, D. Sensharma, and R. L. Whetten, *J. Phys. Chem.*, **94**, 8630 (1990).

25) S. H. Gallagher, R. S. Armstrong, P. A. Lay, and C. A. Reed, *J. Phys. Chem.*, **99**, 5817 (1995).

26) M. R. Wasielewski, M. P. O'Neil, K.R. Lykke, M. J. Pellin, and D. M. Gruen, *J. Am. Chem. Soc.*, **113**, 2774 (1991).

27) K. Tanigaki, T. W. Ebbesen, and S. Kuroshima, *Chem. Phys. Lett.*, **185**, 189 (1991).

28) N. M. Dimitrijevic and P. V. Kamat, *J. Phys. Chem.*, **96**, 4811 (1992).

29) H. T. Etheridge and R. B. Weisman, *J. Phys. Chem.*, **99**, 27822 (1995).

30) T. Kato, T. Kodama, T. Shida, T. Nakagawa, Y. Matsui, S. Szuki, H. Shiromaru, K. Yamauchi, and Y. Achiba, *Chem. Phys. Lett.*, **180**, 446 (1991).

31) M. A. Greaney and S. M. Gorun, *J. Phys. Chem.*, **95**, 7142 (1991).

32) D. R. Lawson, D. L. Feldheim, C. A. Foss, P. K. Dorhout, C. M. Elliott, C. R. Martin, and B. Parkinson, *J. Phys. Chem.*, **96**, 7175 (1992).

33) S. Gorun, M. Greaney, V. Day, C. Day, R. Upton, and C. Briant, in "Fullerenes," ACS Symposium Series, Vol. 481, ed by G. Hammond and V. Kuck, American Chemical Society, Washington, D.C. (1992), pp. 41—53.

34) H. Hase and Y. Miyataka, *Chem. Phys. Lett.*, **215**, 141 (1993).

35) D. M. Guldi, H. Hungerbuhler, E. Janata, and K.-D. Asmus, *J. Phys. Chem.*, **97**, 11258 (1993).

36) M. Mataga, *Adv. Chem.*, **228**, 6 (1991).

37) D. Rehm and A. Weller, *Isr. J. Chem.*, **8**, 259 (1970).

38) R. R. Hung and J. J. Grabowski, *J. Phys. Chem.*, **95**, 6073 (1991).

39) P. M. Allemand, A. Koch, F. Wudl, Y. Rubin, F. Diederich, M. M. Alvarez, S. J. Anz, and R. L. Whetten, *J. Am. Chem. Soc.*, **113**, 1050 (1991).

40) K. C. Hwang and D. Mauzerall, *Nature*, **361**, 138 (1993).

41) R. V. Bensasson, T. Hill, C. Lambert, E. J. Land, S. Leach, and T. G. Truscott, *Chem. Phys. Lett.*, **206**, 197 (1993).