Laser Flash Photolysis Study on Photochemical Generation of Radical Cations of Fullerenes C_{60}, C_{70}, and C_{76}

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Photochemical oxidation processes of fullerenes C_{60}, C_{70}, and C_{76} were examined with a nanosecond laser flash photolysis by observing the transient absorption spectra in the near-IR region. Using tetracyanoethylene as an electron acceptor for fullerenes in the triplet states, the transient absorption bands ascribable to their radical cations were observed. In the solution containing tetracyanoquinodimethane or chloranil as an acceptor, on the other hand, generation of the radical cation was not observed. The difference in these acceptor abilities can be explained on the basis of the free energy changes for the reactions. Photosensitized oxidation of the fullerenes in the presence of cosensitizer was also examined. In the case of C_{70}, oxidation occurred effectively by this reaction; the radical cation of C_{70} appeared immediately after the laser irradiation. C_{76} also showed transient absorption attributed to its radical cation, while the generation rate was smaller than those of C_{60} and C_{70}.

Introduction

Ever since the discovery of C_{60},[1] fullerenes have been one of the most attractive research subjects in experimental and theoretical chemistry. Photophysical processes of C_{60} and C_{70} have been well established by the studies using pico- and nanosecond laser flash photolysis.[2] Photochemical reactions of C_{60} and C_{70}, which act as electron acceptors in their excited states, are investigated by many research groups.[3] Generation of radical cations of C_{60} and C_{70} is also confirmed by using several experimental techniques such as laser flash photolysis,[4] pulse radiolysis,[5] and time-resolved EPR.[6] Compared with C_{60} and C_{70}, however, the study on the photophysical and photochemical properties of higher fullerenes, such as C_{76} and C_{82}, is rare. Recently, we reported the laser flash photolysis study on C_{76}.[7] Its excitation and relaxation processes were elucidated by observing generation and decay of the absorption bands due to the triplet state. It was also confirmed that C_{76} acts as an electron acceptor in its excited state as in the cases of C_{60} and C_{70}: Generation of the radical anion of C_{76} was observed in the photoinduced electron-transfer reaction using *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD) as an electron donor.

One of the noticeable properties of C_{76} is lower oxidation potential (1.12 V vs SCE) than those of C_{60} (1.57 V) and C_{70} (1.51 V).[8] Taking the low oxidation potential of C_{76} into account, generation of the radical cation of C_{76} would be also anticipated by using an adequate electron acceptor in the photoinduced electron-transfer reaction. Recently, Bolskar et al. succeeded in synthesis and isolation of the carbocation of C_{76} using a new oxidizing reagent, $[Ar_3N^{\bullet+}][CB_{11}H_6Br_6^-]$.[9] Their success is the first demonstration of the isolation of fullerene carbocation and indicates stability in its cation form.

In the present paper we reported generation of the radical cations of fullerenes such as C_{60}, C_{70}, and C_{76} by applying two kinds of photoinduced electron-transfer reactions: One is the electron transfer from excited fullerenes to an appropriate electron acceptor, and the other is the electron transfer by cosensitization which was applied to C_{60} by Nonell et al.[4b]

Experimental Section

Materials. Synthesis and purification procedures of C_{76} (D_2) were reported in the previous report and references therein.[7] The concentration of C_{76} in the sample solution was estimated using the extinction coefficient reported for CH_2Cl_2 solution.[10] C_{60} and C_{70} were purchased from Texas Fullerenes Corp. Tetracyanoethylene (TCNE) was purchased from Nacalai Tesque and purified by recrystallization from CH_2Cl_2. *N*-Methylacridinium hexafluorophosphate (NMA^+) was synthesized by the procedure reported by Gebert et al.[11] Other chemicals were of the best commercial grade available.

Apparatus. The nanosecond time-resolved absorption spectra were measured using SHG (532 nm) or THG (355 nm) of a Nd:YAG laser (Quanta-Ray, GCR-130, fwhm 6 ns) as the excitation source. A pulsed xenon flash lamp (Tokyo Instruments, XF80-60) was used as the monitoring light. A Ge-APD module (Hamamatsu Photonics, C5331-SPL) attached to a monochromator (Ritsu MC-10N) was employed as the detector for the spectra in the near-IR region (600−1600 nm). The output signal from the detector was recorded with a digitizing oscilloscope (Hewlett-Packerd 55410B) and analyzed using a personal computer.[3f] The decay lifetimes of fullerenes were estimated using a xenon lamp and a photomultiplier as the monitoring light and the detector, respectively. All the samples for the laser flash photolysis were deaerated by argon bubbling for 15 min in a 1 cm quartz cell.

Steady-state absorption spectra were recorded on a JEOL V-570 UV/vis/near-IR spectrophotometer. Optical path length of a quartz cell for the measurements was 2 mm.

Results and Discussion

Ground-State Absorption Spectra of the Mixture Solution of C_{76} and TCNE. In the present paper, chloranil (CA),

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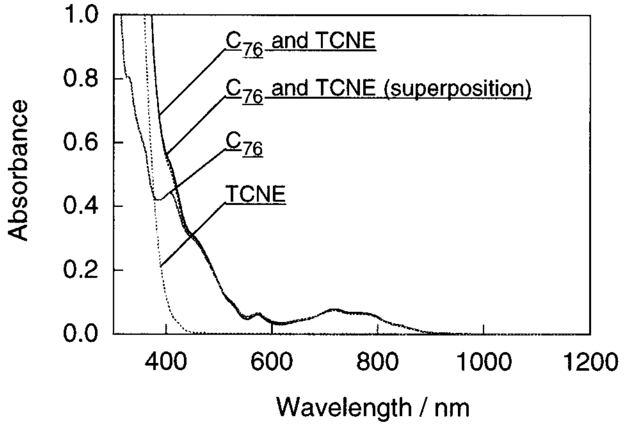

Figure 1. Absorption spectra of C_{76} (0.1 mM), TCNE (10 mM), superposition, and mixture in benzonitrile.

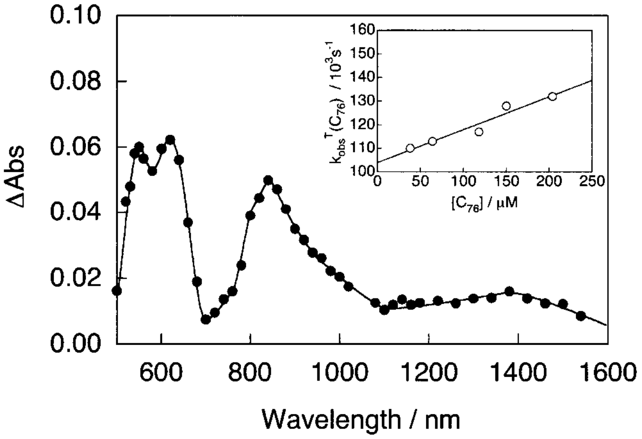

Figure 2. Transient absorption spectrum of 0.1 mM C_{76} toluene solution at 100 ns after laser excitation (SHG of Nd:YAG laser). Insert: dependence of decay rate constant, $k_{obs}{}^T(C_{76})$, on the concentration of C_{76}.

tetracyanoquinodimethane (TCNQ), and TCNE were used as electron acceptors. The reduction potentials of these acceptors are reported to be 0.02, 0.13, and 0.24 V vs SCE, respectively.[12,13] TCNE and TCNQ were examined by Nadtochenko et al. as acceptors for oxidation of excited C_{60}.[4a] They reported that formation of charge-transfer complex of C_{60} and TCNE or TCNQ was not confirmed in the examined concentration ranges ($[C_{60}] < 0.4$ mM, $[TCNE] < 0.24$ M, $[TCNQ] < 7$ mM). In the case of C_{76} (0.1 mM) and TCNE (10 mM), the absorption spectrum of a mixture solution corresponded well to the superposition of those components, indicating that a charge-transfer complex in the ground state is not formed or can be negligible under the present experimental conditions (Figure 1).

T−T Absorption of C_{76} in the Near-IR Region. It has been reported that many photoinduced reactions of C_{60} and C_{70} proceed via their triplet excited states.[3] However, there are only a few reports on characterization of the triplet excited state of C_{76} ($^TC_{76}{}^*$).[7,14] Here, the lifetime of $^TC_{76}{}^*$ was estimated by taking some quenching processes into consideration.

Absorption bands that can be attributed to $^TC_{76}{}^*$ appeared in the near-IR region immediately after the laser irradiation (Figure 2). The transient absorption of $^TC_{76}{}^*$ is quite weak even by the laser excitation at high laser intensity (ca. 60 mJ/pulse, SHG) despite the large extinction coefficient of $^TC_{76}{}^*$.[7] The finding suggests a low quantum yield of the intersystem crossing process of the excited C_{76} as indicated by the time-resolved EPR study.[14] The absorption−time profile of $^TC_{76}{}^*$ can be analyzed by the first-order decay function, indicating that the triplet−triplet (T−T) annihilation process is negligible in the deactivation process of $^TC_{76}{}^*$, while the T−T annihilation is apparent in the cases of $^TC_{60}{}^*$ and $^TC_{70}{}^*$ under high laser power excitation. The negligible T−T annihilation of $^TC_{76}{}^*$ is in accord with the small quantum yield of the intersystem crossing process. The first-order decay rate constant of $^TC_{76}{}^*$, $k_{obs}{}^T(C_{76})$, increased with the concentration of C_{76} in the ground state (Figure 2). The good linearity between them indicates deactivation of $^TC_{76}{}^*$ by a self-quenching process (eq 1).

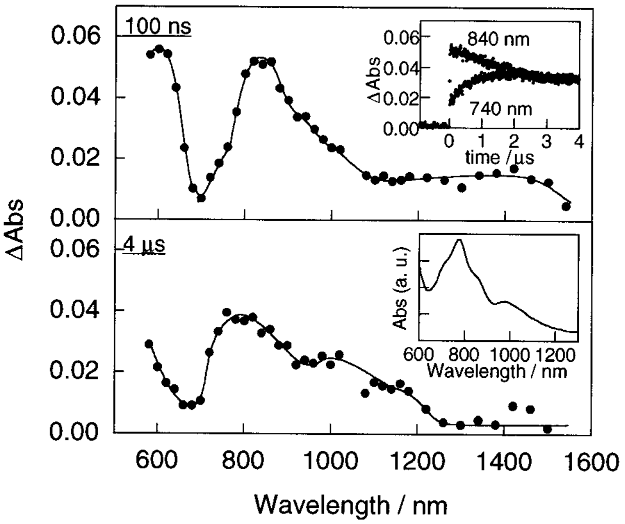

Figure 3. Transient absorption spectra of benzonitrile solution containing 0.1 mM C_{76} and 4 mM TCNE at (upper) 100 ns and (lower) 4 μs after laser excitation. Excitation: SHG of Nd:YAG laser. Insert: (upper) absorption−time profiles at 740 and 840 nm; (lower) absorption spectrum of $C_{76}{}^{\bullet+}$ generated chemically (from ref 9).

$$^TC_{76}{}^* + C_{76} \rightarrow 2C_{76} \qquad (1)$$

The bimolecular rate constant of the self-quenching process, $k_{sq}(C_{76})$,was estimated to be 1.4×10^8 M^{-1} s^{-1} from the slope of the line of Figure 2. The estimated rate constant is similar to those of $^TC_{60}{}^*$ (2×10^8 M^{-1} s^{-1}) and $^TC_{70}{}^*$ (6×10^8 M^{-1} s^{-1}).[2e] The intercept of the straight line of Figure 2 is 1.04×10^5 s^{-1}, which corresponds to 9.6 μs of the intrinsic lifetime of $^TC_{76}{}^*$. The intrinsic lifetime is quite short compared with the reported values for $^TC_{60}{}^*$ and $^TC_{70}{}^*$ (250 μs for both).[2e]

Photochemical Generation of Radical Cations of Fullerenes in the Presence of Electron Acceptors. *Oxidation of Fullerenes by TCNE.* When the benzonitrile solution containing C_{76} and TCNE was irradiated by the 532 nm laser, the transient absorption bands that can be attributed to $^TC_{76}{}^*$ appeared immediately after the irradiation. The absorption bands due to $^TC_{76}{}^*$ decayed within a few microseconds, and new absorption bands appeared at 1100 (sh), 980, 780, and <600 nm, exhibiting the rising absorption−time profile (Figure 3 and its insert). From the comparison with the absorption spectrum of $C_{76}{}^{\bullet+}$ which was generated chemically by treating with $[Ar_3N^{\bullet+}][CB_{11}H_6Br_6{}^-]$ (insert of Figure 3),[9] the new transient absorption bands can be attributed to $C_{76}{}^{\bullet+}$, although the absorption maximum at 780 nm was somewhat deformed by the depletion of ground-state absorption of C_{76} around 700 nm. Since 532 nm light excites C_{76} only (Figure 1), it can be reasonably concluded that $C_{76}{}^{\bullet+}$ was generated by the electron-transfer reaction from $^TC_{76}{}^*$ to TCNE (eq 2). The radical anion of TCNE ($TCNE^{\bullet-}$) is reported to appear around 440 nm, which is difficult to observe because of the strong ground-state absorption of C_{76}.

$$^TC_{76}{}^* + TCNE \rightarrow C_{76}{}^{\bullet+} + TCNE^{\bullet-} \qquad (2)$$

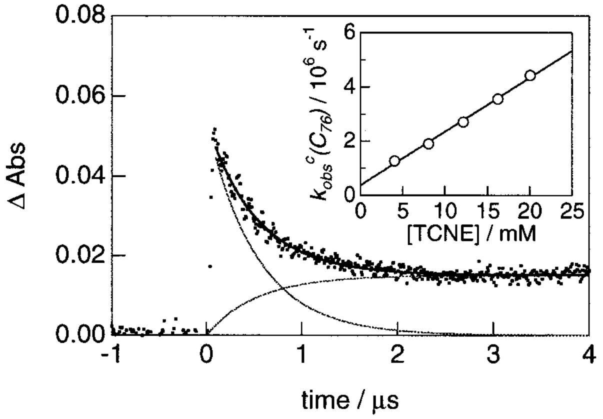

Figure 4. Absorption−time profile at 600 nm observed in benzonitrile solution containing 0.1 mM C_{76} and 8 mM TCNE excited with SHG of Nd:YAG laser. Solid lines are fitting curves obtained by assuming decay of $^{T}C_{76}^{*}$ and rising of $C_{76}^{\bullet +}$. Insert: dependence of rate constants of the generation of $C_{76}^{\bullet +}$, $k_{obs}^{c}(C_{76})$, on the concentration of TCNE.

TABLE 1: Triplet Lifetimes and Bimolecular Rate Constants of $^{T}C_{n}^{*}$ (n = 60, 70, 76)

	C_{60}	C_{70}	C_{76}
τ_T (μs)	250[a]	250[a]	9.6
k_{sq} (M^{-1} s^{-1})	2×10^8 [a]	6×10^8 [a]	1.4×10^8
k_{qT} for CA (M^{-1} s^{-1})	n.r.[b]	n.r.	n.r.
k_{qT} for TCNQ (M^{-1} s^{-1})	2.5×10^9	3.1×10^9	$<10^8$
k_{qT} for TCNE (M^{-1} s^{-1})	3.9×10^8	1.2×10^9	2.0×10^8

[a] From ref 2e. [b] n. r. = no reaction.

The transient absorption bands of $C_{76}^{\bullet +}$ are overlapped with those of $^{T}C_{76}^{*}$ in almost all examined spectral region. Therefore, the rate constants of the decay of $^{T}C_{76}^{*}$ and the generation of $C_{76}^{\bullet +}$ were estimated by applying the following relation (eq 3)

$$\Delta \mathrm{Abs} = C_1 \exp(-k_{obs}^{T}(C_{76})t) + C_2(1 - \exp(-k_{obs}^{c}(C_{76})t)) \quad (3)$$

where C_1 and C_2 are the maximal absorbance of $^{T}C_{76}^{*}$ and $C_{76}^{\bullet +}$; $k_{obs}^{T}(C_{76})$ and $k_{obs}^{c}(C_{76})$ are rate constants of the decay of $^{T}C_{76}^{*}$ and the generation of $C_{76}^{\bullet +}$, respectively. In this relation it was assumed that $k_{obs}^{c}(C_{76})$ is much larger than decay rate constant of the generated radical cation. One of the fitting curves according to eq 3 is shown in Figure 4. In the insert, estimated rate constants, $k_{obs}^{c}(C_{76})$, are plotted against the concentration of TCNE. From the linear relationship between them, a bimolecular rate constant of the quenching of $^{T}C_{76}^{*}$, $k_{qT}(C_{76})$, was estimated to be 2.0×10^8 M^{-1} s^{-1}.

In the case of C_{60}, it was reported that the laser irradiation to the benzonitrile solution containing C_{60} and TCNE generated the absorption band at 980 nm, which was ascribable to the radical cation of C_{60} ($C_{60}^{\bullet +}$).[4a] We also observed the generation of $C_{60}^{\bullet +}$ in the C_{60} and TCNE system at almost the same bimolecular rate constant with the reported value (Table 1). The estimated rate constant was similar to that of C_{76}.

Decay of the transient absorption band of $C_{76}^{\bullet +}$ can be attributed mainly to the back-electron-transfer reaction (eq 4).

$$C_{76}^{\bullet +} + \mathrm{TCNE}^{\bullet -} \rightarrow C_{76} + \mathrm{TCNE} \quad (4)$$

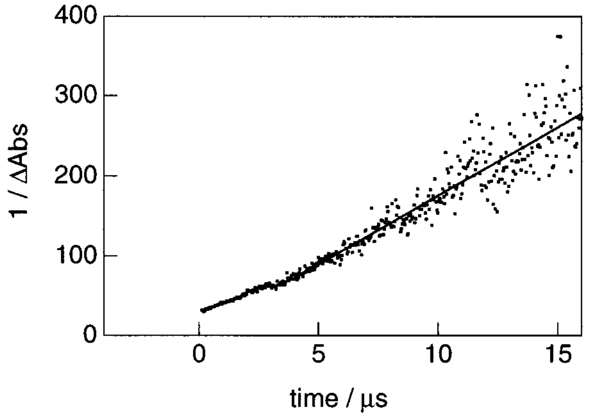

Figure 5. Second-order plot for the decay at 600 nm observed in benzonitrile solution containing 0.1 mM C_{76} and 20 mM TCNE excited with SHG of Nd:YAG laser.

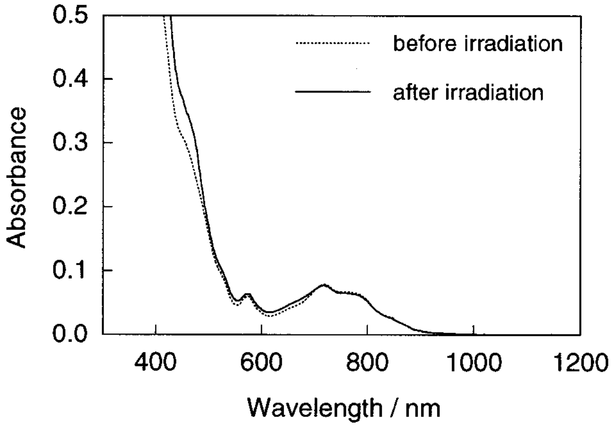

Figure 6. Absorption spectra of benzonitrile solution containing 0.1 mM C_{76} and 10 mM TMPD before and after several hundreds shots of laser irradiation (SHG of Nd:YAG laser).

The second-order plot of the absorption−time profile at 600 nm is shown in Figure 5. The initial part is due to the decay of $^{T}C_{76}^{*}$, and the latter part is due to the back-electron-transfer reaction. From the straight line obtained from the latter part of Figure 5, k_{bet}/ϵ_{600}, where k_{bet} and ϵ_{600} are the back-electron-transfer rate constant and the extinction coefficient of $C_{76}^{\bullet +}$ at 600 nm, respectively, was estimated to be 1.7×10^7 cm s^{-1}. At the present stage of our study, ϵ_{600} is unknown. However, if we assume ϵ_{600} is to be 10^3 M^{-1} cm^{-1}, which is the same order as that of $C_{76}^{\bullet -}$,[7] 10^{10} M^{-1} s^{-1} of k_{bet} was estimated. From this roughly estimated value, the generated radical ions are expected to return to the corresponding neutral forms at the rate close to the diffusion limit.

The ground-state absorption spectrum of C_{76} and TCNE mixture after several hundreds shots of the laser irradiation is shown in Figure 6. Compared with the spectrum measured before the laser irradiation, absorption increased around 450 nm. One of the plausible origins of the new absorption band is $\mathrm{TCNE}^{\bullet -}$, which is known to be relatively stable.[6] At present, however, we cannot exclude the possibility that the new absorption band is due to an adduct of TCNE with C_{76}.

In the case of the mixture solution of C_{70} and TCNE, transient absorption bands ascribable to the radical cation of C_{70} ($C_{70}^{\bullet +}$) appeared at 940, 820, 740, and 680 nm, after the decay of the absorption band of $^{T}C_{70}^{*}$ at 980 nm. The 940 and 820 nm bands are in good agreement with the transient absorption bands of $C_{70}^{\bullet +}$ at 930 and 830 nm observed by the pulse radiolysis experiments in 1,2-dichloroethane.[5b] The bimolecular rate constant of the quenching of $^{T}C_{70}^{*}$, $k_{qT}(C_{70})$, was estimated to be 1.2×10^9 M^{-1} s^{-1} from the decaying absorption−time profile at 980 nm. The estimated $k_{qT}(C_{70})$ is close to the diffusion limit, while those of C_{60} and C_{76} are 1 order smaller than the diffusion limit. To estimate the electron-transfer rates from these k_{qT} values, it is necessary to evaluate ϵ of the triplet states and the radical cations. However, the ϵ values of the radical cations of fullerenes have not been reported yet.

Fullerenes and CA. When the mixture solution of CA and C_{76} was irradiated by the 532 nm laser, the transient absorption bands ascribable to ${}^{T}C_{76}{}^{*}$ appeared immediately after the laser irradiation. However, the decay of ${}^{T}C_{76}{}^{*}$ was not accelerated in the presence of CA. This finding indicates that CA does not act as an electron acceptor or a triplet energy acceptor for ${}^{T}C_{76}{}^{*}$. The triplet energy of C_{76} is considered to be lying between 92 and 106 kJ mol^{-1} from the reduction potentials of the electron acceptors, the oxidation potential of C_{76}, and the results of the energy-transfer reaction in the previous paper.[7] In the cases of C_{60} and C_{70}, the transient absorption bands of their triplet excited states were also not quenched in the presence of CA. These findings also indicate that CA is not an electron acceptor or a triplet energy acceptor for ${}^{T}C_{60}{}^{*}$ and ${}^{T}C_{70}{}^{*}$. The acceptor ability of CA can be explained on the basis of the free energy changes on the reactions estimated by using the Rehm−Weller relation;[15] for C_{60} and C_{70}, −3.9 and −8.7 kJ mol^{-1} of free energy changes are calculated, respectively, while −25.1 and −29.9 kJ mol^{-1} of sufficient negative values are expected for the reactions with TCNE.

Photoinduced Reaction between Fullerenes and TCNQ. In the laser flash photolysis experiment on the mixture solution of C_{60} and TCNQ, Nadtochenko et al. observed quenching of ${}^{T}C_{60}{}^{*}$, but generation of $C_{60}{}^{\bullet+}$ was not observed.[4a] They attributed the photoinduced reactions to exciplex formation and triplet energy transfer from ${}^{T}C_{60}{}^{*}$ to TCNQ due to the lower triplet energy of TCNQ (<1 eV).[16] In the case of the mixture of TCNQ and C_{70} or C_{76}, the 532 nm laser excitation also resulted in the quenching of their triplet states. The evidence for the generation of the radical cations of C_{70} and C_{76} was not obtained. As quenching mechanisms of ${}^{T}C_{70}{}^{*}$ and ${}^{T}C_{76}{}^{*}$ by TCNQ, participation of the exciplex formation and/or the energy transfer reaction is expected. The bimolecular rate constants estimated for the quenching reaction of ${}^{T}C_{60}{}^{*}$, ${}^{T}C_{70}{}^{*}$, and ${}^{T}C_{76}{}^{*}$ by TCNQ are summarized in Table 1. In the cases of C_{60} and C_{70}, triplet excited states deactivated at rates close to the diffusion-controlled rate. As for C_{76} the rate constant is small compared with those of C_{60} and C_{70}. One of the reasons for the small rate constant will be the small triplet energy of C_{76}, insufficient for the energy transfer to TCNQ.

Generation of Radical Cations of Fullerenes by Photosensitized Electron Transfer. Nonell et al. reported that $C_{60}{}^{\bullet+}$ was generated in high yield by photosensitized electron-transfer reaction using a cosensitizer at high concentration.[4b] Using NMA^{+} and biphenyl (BP) as the sensitizer and the cosensitizer, respectively, $C_{60}{}^{\bullet+}$ was generated by following reaction scheme (eq 5).

$$
\begin{aligned}
{}^{S}(NMA^{+})^{*} + BP &\rightarrow NMA^{\bullet} + BP^{\bullet+} \\
BP^{\bullet+} + C_{60} &\rightarrow BP + C_{60}{}^{\bullet+} \qquad (5)
\end{aligned}
$$

Here, we applied this reaction to oxidation of C_{70} and C_{76}. From the oxidation potentials of C_{70} and C_{76}, the oxidation reactions by cosensitization would be also anticipated. THG (355 nm) of the Nd:YAG laser was applied to the excitation of NMA^{+}.

The transient absorption spectra obtained by the 355 nm laser excitation to benzonitrile solution containing 0.2 mM C_{70}, 0.2 mM NMA^{+}, and 200 mM BP are shown in Figure 7a. The absorption bands ascribable to $C_{70}{}^{\bullet+}$ appeared clearly at 980, 940, 820, and 720 nm. When $C_{70}{}^{\bullet+}$ was generated by the electron-transfer reaction with TCNE, the absorption peaks at 800∼1000 nm were difficult to distinguish from those of ${}^{T}C_{70}{}^{*}$ because of weak absorption probably due to low quantum yield of the radical generation. When the solution was excited with SHG (532 nm), which excites C_{70} only, the radical formation was not confirmed. This finding supports the reaction by eq 5. In the case of THG excitation, the absorption bands of $C_{70}{}^{\bullet+}$ appeared immediately after the laser irradiation, while $BP^{\bullet+}$, which shows an absorption band at 680 nm (Figure 7b),[17] was not observed as shown in Figure 7a, indicating that the generation of $C_{70}{}^{\bullet+}$ by eq 5 is a fast process.

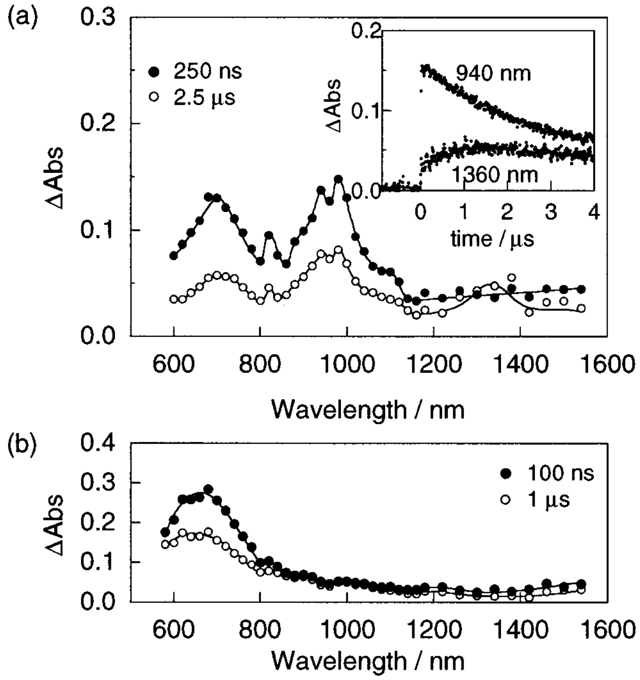

Figure 7. (a) Transient absorption spectra of benzonitrile solution containing 0.2 mM C_{70}, 0.2 mM NMA^{+}, and 200 mM BP. Excitation: THG of Nd:YAG laser. Insert: absorption−time profiles at 940 and 1360 nm. (b) Transient absorption spectra of benzonitrile solution containing 0.2 mM NMA^{+} and 200 mM BP.

It is interesting to note that a new absorption band appeared at 1360 nm with rising absorption−time profile. It is well-known that the radical anion of C_{70} ($C_{70}{}^{\bullet-}$) shows the characteristic absorption band at 1360 nm. Therefore, one of the possible origins of the new absorption band at 1360 nm in Figure 7a is $C_{70}{}^{\bullet-}$ generated by the electron-transfer reaction between $NMA^{\bullet}$ and ${}^{T}C_{70}{}^{*}$ or C_{70}. In the case of the photosensitized reaction of C_{60}, a weak absorption band of the radical anion of C_{60} ($C_{60}{}^{\bullet-}$) was also observed at 1080 nm in addition to the strong absorption band of $C_{60}{}^{\bullet+}$ (980 nm).

When the mixture solution of C_{76}, NMA^{+}, and BP was irradiated by a 355 nm laser, the transient absorption bands ascribable to $C_{76}{}^{\bullet+}$ appeared with decrease in the absorption band of $BP^{\bullet+}$. The generation of $C_{76}{}^{\bullet+}$ can be attributed to the photosensitized electron-transfer reaction, eq 5. From the decay of $BP^{\bullet+}$, the bimolecular rate constant of the reaction was estimated to be 1.5×10^{9} M^{-1} s^{-1}, which is smaller than that of C_{60}, 2×10^{10} M^{-1} s^{-1}. This tendency is the same with the photochemical reduction of fullerenes by TMPD. In the cases of the reactions with TMPD, 1×10^{10} and 8×10^{9} M^{-1} s^{-1} bimolecular rate constants were estimated for C_{60} and C_{70}, respectively, while that of C_{76} was 8×10^{8} M^{-1} s^{-1}, which is 1 order smaller than the diffusion-controlled rate.

The lifetimes of the radical cations of C_{60}, C_{70}, and C_{76} were estimated to be 3.0, 4.6, and 14.0 μs, respectively, by applying the first-order decay function. It is interesting to note that the lifetime of fullerene increases with its size, indicating stability of the generated radical cations.

Conclusion

Photochemical oxidation reactions of fullerenes C_{60}, C_{70}, and C_{76} were examined by two kinds of electron-transfer processes. Electron transfers from the excited fullerenes to the electron acceptor were confirmed when TCNE was used as an acceptor, while CA and TCNQ did not act as an oxidizing reagent because of insufficient reduction potential of acceptor and/or predominant energy-transfer process than the electron transfer. Generation of radical cations of fullerenes by cosensitization was also confirmed. In the both processes, the reactions of C_{76} did not proceed as fast as those of C_{60} and C_{70}. This tendency is the same with the photochemical reduction of fullerenes. The reason for the low reactivity of C_{76} in excited states is not clear at the present stage of our study. Studies on the photochemical reactions of the more higher fullerenes are in progress.

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References and Notes

(1) Kroto, H. W.; Heath, J. R.; O’Brien, S. C.; Curl, R. F.; Smally, R. E. *Nature* **1985**, *318*, 162.

(2) (a) Arbogast, J. W.; Darmanyan, A. P.; Foote, C. S.; Rubin, Y.; Diederich, F. N.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Phys. Chem.* **1991**, *95*, 11. (b) Ebbesen, T. W.; Tanigaki, K.; Kuroshima, S. *Chem. Phys. Lett.* **1991**, *181*, 501. (c) Arbogast, J. W.; Foote, C. S. *J. Am. Chem. Soc.* **1991**, *113*, 8886. (d) Tanigaki, K.; Ebbesen, T. W.; Kuroshima, S. *Chem. Phys. Lett.* **1991**, *185*, 189. (e) Dimitrijevic, N. M.; Kamat, P. V. *J. Phys. Chem.* **1992**, *96*, 4811. (f) Palit, D. K.; Sapre, A. V.; Mittal, J. P. *Chem. Phys. Lett.* **1992**, *195*, 1. (g) Kim, D.; Lee, M.; Suh, Y. D.; Kim, S. K. *J. Am. Chem. Soc.* **1992**, *114*, 4429. (h) Sun, Y.-P.; Wang, P.; Hamilton, N. B. *J. Am. Chem. Soc.* **1993**, *115*, 6378. (i) Watanabe, A.; Ito, O.; Watanabe, M.; Saito, H.; Koishi, M. *J. Phys. Chem.* **1996**, *100*, 10518.

(3) (a) Sension, R. J.; Szarka, A. Z.; Smith, G. R.; Hochstrasser, R. M. *Chem. Phys. Lett.* **1991**, *185*, 179. (b) Osaki, T.; Tai, Y.; Yazawa, M.; Tanemura, S.; Inukai, K.; Ishiguro, K.; Sawaki, Y.; Saito, Y.; Shinohara, H.; Nagashima, H. *Chem. Lett.* **1993**, 789. (c) Nonell, S.; Arbogast, J. W.; Foote, C. S. *J. Phys. Chem.* **1992**, *96*, 4169. (d) Ghosh, H. N.; Pal, H.; Sapre, A. V.; Mittal, J. P. *J. Am. Chem. Soc.* **1993**, *115*, 11722. (e) Dimitrijevic, N. M.; Kamat, P. V. *J. Phys. Chem.* **1992**, *96*, 4811. (f) Watanabe, A.; Ito, O. *J. Phys. Chem.* **1994**, *98*, 7736. (g) Ito, O.; Sasaki, Y.; Yoshikawa, Y.; Watanabe, A. *J. Phys. Chem.* **1995**, *99*, 9838. (h) Schaffner, E.; Fischer, H. *J. Phys. Chem.* **1993**, *97*, 13149.

(4) (a) Nadtochenko, V. A.; Denisov, N. N.; Rubtsov, I. V.; Lobach, A. S.; Moravskii, A. P. *Chem. Phys. Lett.* **1993**, *208*, 431. (b) Nonell, S.; Arbogast, J. W.; Foote, C. S. *J. Phys. Chem.* **1992**, *96*, 4169.

(5) (a) Guldi, D. M.; Hungerbühler, H.; Janata, E.; Asmus, K.-D. *J. Phys. Chem.* **1993**, *97*, 11258. (b) Guldi, D. M.; Hungerbühler, H.; Wilhelm, M.; Asmus, K.-D. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1391.

(6) Michaeli, S.; Meiklyar, V.; Schulz, M.; Möbius, K.; Levanon, H. *J. Phys. Chem.* **1994**, *98*, 7444.

(7) Fujitsuka, M.; Watanabe, A.; Ito, O.; Yamamoto, K.; Funasaka, H. *J. Phys. Chem. A* **1997**, *101*, 4840.

(8) Yang, Y.; Arias, F.; Echegoyen, L.; Chibante, L. P. F.; Flanagan, S.; Robertson, A.; Wilson, L. J. *J. Am. Chem. Soc.* **1995**, *117*, 7801.

(9) Bolskar, R. D.; Mathur, R. S.; Reed, C. A. *J. Am. Chem. Soc.* **1996**, *118*, 13093.

(10) Ettl, R.; Chao, I.; Diederich, F.; Whetten, R. L. *Nature* **1991**, *353*, 149.

(11) Gebert, H.; Regenstein, W.; Bendig, J.; Kreysig, D. *Z. Phys. Chem.* (*Munich*) **1982**, *263*, 65.

(12) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401.

(13) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods;* Wiley: New York, 1980.

(14) Terazima, M.; Hirota, N.; Shinohara, H.; Asato, K. *Electrochem. Soc. Proc.* **1995**, *95*−*10*, 267.

(15) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

(16) (a) Lowitz, D. A. *J. Chem. Phys.* **1967**, *46*, 4698. (b) Bieber, A.; Andre, J. J. *Chem. Phys.* **1974**, *5*, 166.

(17) Shida, T. *Electronic Absorption Spectra of Radical Ions*; Elsevier: Amsterdam, 1988.