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ARTICLES

Laser Flash Photolysis Study of Photophysical and Photochemical Properties of a Higher Fullerene, C_{76}

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Photophysical and photochemical properties of C_{76} have been investigated by using nano- and picosecond laser flash photolysis methods. In the nanosecond laser flash photolysis of C_{76}, transient absorption ascribable to the triplet excited state of C_{76} ($^{T}C_{76}^{*}$) was observed in the visible and near-IR regions. From the generation of the absorption band of $^{T}C_{76}^{*}$, the lifetime of the singlet excited state was estimated to be 1.7 ns. Under the presence of β-carotene in toluene, $^{T}C_{76}^{*}$ was deactivated by energy transfer to β-carotene at a 2.6×10^{9} M^{-1} s^{-1} rate constant. Electron-transfer reaction to $^{T}C_{76}^{*}$ was also confirmed in a benzonitrile solution containing C_{76} and tetramethyl-*p*-phenylenediamine (TMPD) as an electron donor. A bimolecular rate constant for quenching of $^{T}C_{76}^{*}$ by TMPD was estimated to be 7.8×10^{8} M^{-1} s^{-1}.

Introduction

Since the advent of the procedure for large scale synthesis of fullerenes,[1] quite a large number of studies have been carried out for the clarification of their basic properties and for their applications. Photophysical and photochemical properties of fullerenes have been also widely investigated. The excitation−relaxation processes of C_{60} and C_{70} have been well established by studies using nano- and picosecond laser flash photolysis techniques.[2] From the viewpoint of photochemistry, C_{60} and C_{70} are good electron acceptors and many photoinduced reactions have been reported by using these fullerenes as acceptors.[3] For example, generations of adducts of C_{60} have been observed in laser photolysis studies with anthracene[4a] and with tetraethoxyethene.[4b] It is also reported that doping of fullerenes to polymer films such as polyvinylcarbazole and poly(*p*-phenylene vinylene) results in the enhancement of photoconductivity.[5]

The synthesis by evaporation of a graphite rod under inert gas also generates fullerenes of higher molecular weight, such as C_{76} and C_{82}, as minor products. For C_{76}, isolation from Krätschmer−Huffman soot was reported by Diederich et al. in 1991.[6] ^{13}C NMR study of C_{76} indicated a structure of D_2 symmetry, which is one of the two candidate structures (D_2 and T_d symmetries) predicted by Manolopoulos based on the isolated-pentagon rule.[7,8] Additionally, chirality has been expected for C_{76}. Hawkins and Meyer demonstrated kinetic resolution of racemic C_{76} by asymmetric osmylation.[9] Basic properties of C_{76} have been revealed recently by several experimental techniques: IR and Raman spectroscopy,[10] cyclic voltammetry,[11] photoelectron spectroscopy,[12] electron energy loss spectroscopy,[13] and so on. Structures in the solid phase and on surfaces were investigated by transmission electron microscopy and scanning tunneling microscopy, respectively.[14,15] In the electrochemical study, C_{76} showed reversible oxidative and reductive waves, in contrast to C_{60} and C_{70}, which show irreversible oxidative waves.[11a] This indicates the stability in its radical cation form. Thus, C_{76} is expected to behave as an electron donor as well as an electron acceptor. However, no attempt has been made to generate the radical cation or anion of C_{76} photochemically. Furthermore, its excited state behavior has not been well understood. Very recently, the triplet excited state was characterized by the time-resolved EPR method.[16] In the present paper we reported nano- and picosecond laser flash photolysis study of C_{76} in the visible and near-IR regions. Transient absorption bands that can be attributed to the triplet excited state were observed. Furthermore, the electron-transfer reaction and energy-transfer reaction of C_{76} were also reported.

Experimental Section

Materials. C_{76} was synthesized by evaporating a graphite rod using a contact arc method and purified by using an HPLC system. Details of the HPLC procedure are described in previous reports.[17] To remove fullerene oxides from C_{76}, the chromatographic purification procedure was performed at two temperatures (0 and 45 °C). Identification of the sample was carried out using a positive- and negative-ion Fourier transform ion cyclotron resonance mass spectrometer. The concentration of C_{76} in the sample solution was estimated using the extinction coefficient reported for CH_2Cl_2 solution.[7] C_{76} radical anion ($C_{76}^{\bullet -}$) at 77 K was generated by γ irradiation (^{60}Co) to C_{76} saturated methyltetrahydrofuran (MTHF) solution for 8.2 h at 2.4×10^{4} R h^{-1}.[18a] MTHF was purified according to the reported procedure.[18b] *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD) was prepared from TMPD dihydrochloride (Kanto Kagaku) by reduction just before use. Other chemicals were of the best commercial grade available.

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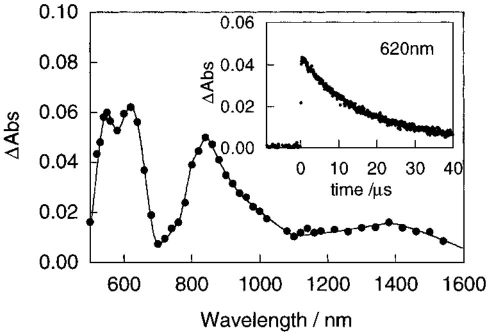

Figure 1. Transient absorption spectrum of 0.1 mM C_{76} toluene solution at 100 ns after laser excitation (SHG of Nd:YAG laser). The insert shows the absorption−time profile at 620 nm.

Apparatus. The nanosecond time-resolved absorption spectra were measured using second harmonic generation (SHG) (532 nm) or third harmonic generation (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 Si PIN photodiode (Hamamatsu Photonics, S1722-02) attached to a monochromator (Ritsu MC-10N) was employed as the detector for the spectra in the visible region (500−1000 nm). For the absorption spectra in the near-IR region (600−1600 nm), a Ge avalanche photodetector (APD) module (Hamamatsu Photonics, C5331-SPL) was used as the detector. The output signal from the detector was recorded with a digitizing oscilloscope (Hewlett-Packerd 55410B) and analyzed using a personal computer.[3f]

The picosecond laser flash photolysis was carried out using SHG (532 nm) of an active/passive mode-locked Nd:YAG laser (Continuum, PY61C-10, fwhm 35 ps) as the excitation light. A white continuum pulse generated by focusing the fundamental of the Nd:YAG laser on a D_2O/H_2O (1:1 volume) cell was used as the monitoring light. The monitoring light transmitted thorough the sample was detected with a dual MOS detector (Hamamatsu Photonics, C6140) equipped with a polychromator (Acton Research, SpectraPro-150). The spectra were obtained by averaging 100 events on a microcomputer. All the samples for the laser flash photolysis were contained in a 1 cm quartz cell and were deaerated by 15 min of argon bubbling.

Steady-state absorption spectra were recorded on a JEOL V-570 UV−vis-NIR spectrophotometer.

Results and Discussion

T−T Absorption of C_{76} in the Visible and Near-IR Regions. The absorption spectrum of C_{76} in CH_2Cl_2 was reported by Ettl et al.[7] In toluene and benzonitrile, essentially the same absorption spectra were observed, and the shift of the peak position was not confirmed. Figure 1 shows a transient absorption spectrum of C_{76} in toluene obtained by the laser flash photolysis excited by SHG of Nd:YAG laser. Clear absorption bands appeared at 840, 620, and 540 nm accompanying a weak and broad absorption band around 1400 nm. Minima observed in the spectrum in Figure 1 correspond well with the peak positions of the ground-state absorption spectrum. Since these absorption bands disappeared in the aerated solution, the absorption bands could be attributed to the triplet excited state of C_{76} ($^{T}C_{76}^{*}$). In contrast to C_{60} and C_{70}, T−T absorption of C_{76} is very weak even by excitation at high laser intensity (532 nm at ca. 60 mJ/pulse). This results from a very low quantum yield of the intersystem crossing, as indicated by the time-resolved EPR study.[16] As in the insert of Figure 1, the transient absorption band of $^{T}C_{76}^{*}$ decayed according to the first-order decay function and the decay rate constant was estimated to be 1.4×10^5 s^{-1} corresponding to 7.1 μs of decay lifetime. The triplet lifetime of C_{76} is short compared with those of C_{60} (>280 μs)[2b] and C_{70} (130 μs).[2c] In benzonitrile, similar transient absorption spectra were observed. After several hundred shots of laser irradiation, no change was confirmed in the ground-state absorption spectra. This result shows that C_{76} is quite stable to laser irradiation as C_{60} and C_{70}.

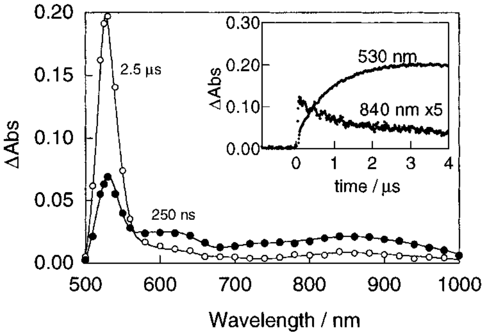

Figure 2. Transient absorption spectra of toluene solution containing 0.06 mM C_{76} and 0.12 mM β-carotene. Excitation is from the SHG of a Nd:YAG laser. The insert shows the absorption−time profiles at 530 and 840 nm.

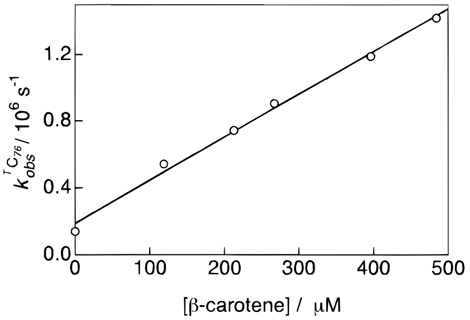

Figure 3. Dependence of $k_{obs}^{TC_{76}}$ on the concentration of β-carotene.

In the presence of β-carotene, the transient absorption bands ascribable to $^{T}C_{76}^{*}$ decayed within a few hundred nanoseconds and a new transient absorption band ascribable to the triplet excited state of β-carotene (^{T}(β-carotene)*) appeared at 530 nm with a rising absorption time profile over about 500 ns (Figure 2). The generation of the absorption band of ^{T}(β-carotene)* can be attributed to triplet energy transfer from $^{T}C_{76}^{*}$, i.e.,

$$^{T}C_{76}^{*} + \beta\text{-carotene} \rightarrow C_{76} + {}^{T}(\beta\text{-carotene})^{*} \qquad (1)$$

From the ground-state absorption edge of C_{76} (920 nm) and the triplet energies of molecular oxygen and β-carotene,[19,20] the triplet energy of C_{76} is considered to be lying between 92 and 130 kJ mol^{-1}. In the presence of β-carotene, the transient absorption bands of $^{T}C_{76}^{*}$ decayed according to the first-order decay function,

$$\Delta\text{Abs} = C_1 \exp(-k_{obs}^{TC_{76}} t) \qquad (2)$$

where C_1 and $k_{obs}^{TC_{76}}$ are constants corresponding to the initial absorbance of $^{T}C_{76}^{*}$ and a pseudo-first-order decay rate constant, respectively. The $k_{obs}^{TC_{76}}$ increased with increasing the concentration of β-carotene. From the dependence of $k_{obs}^{TC_{76}}$ on the concentration of β-carotene, the bimolecular rate constant of the present energy-transfer reaction is estimated to be 2.6×10^9 M^{-1} s^{-1}, close to the diffusion-controlled rate (Figure 3).

The absorption−time profile at 530 nm in Figure 2 includes the decay of $^{T}C_{76}^{*}$ and the generation of ^{T}(β-carotene)* and

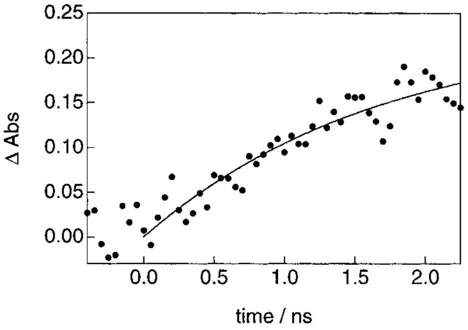

Figure 4. Absorption−time profile at 600 nm observed in toluene solution containing 0.1 mM C_{76} excited with SHG of Nd:YAG laser (fwhm of 35 ps).

can be analyzed by fitting to

$$\Delta\mathrm{Abs} = C_2 \exp\left(-k_{\mathrm{obs}}^{\mathrm{T}C_{76}} t\right) + C_3\left(1 - \exp\left(-k_{\mathrm{obs}}^{\mathrm{T}\beta\mathrm{C}} t\right)\right) \quad (3)$$

where C_2 and C_3 are constants corresponding to the initial absorbance of ${}^{\mathrm{T}}C_{76}^{*}$ and the final absorbance of ${}^{\mathrm{T}}(\beta$-carotene$)^{*}$, respectively, and $k_{\mathrm{obs}}^{\mathrm{T}\beta\mathrm{C}}$ is a pseudo-first-order rate constant for the generation of ${}^{\mathrm{T}}(\beta$-carotene$)^{*}$. From the ratio of C_1 and C_3, the difference of the extinction coefficients of ${}^{\mathrm{T}}C_{76}^{*}$ ($\epsilon_{\mathrm{T}}^{C_{76}} - \epsilon_{0}^{C_{76}}$, where $\epsilon_{\mathrm{T}}^{C_{76}}$ and $\epsilon_{0}^{C_{76}}$ are extinction coefficients of C_{76} in the triplet and in the ground states, respectively) can be estimated based on the difference of the extinction coefficients of ${}^{\mathrm{T}}(\beta$-carotene$)^{*}$ ($\epsilon_{\mathrm{T}}^{\beta\mathrm{C}} - \epsilon_{0}^{\beta\mathrm{C}}$, where $\epsilon_{\mathrm{T}}^{\beta\mathrm{C}}$ and $\epsilon_{0}^{\beta\mathrm{C}}$ are extinction coefficients of β-carotene in the triplet and in the ground states, respectively).[2c,21] Adopting 1.7×10^5 M^{-1} cm^{-1} of $\epsilon_{\mathrm{T}}^{\beta\mathrm{C}}$ for ${}^{\mathrm{T}}(\beta$-carotene$)^{*}$ in cyclohexane solution,[21] 2.0×10^4 M^{-1} cm^{-1} of $\epsilon_{\mathrm{T}}^{C_{76}}$ is estimated at 840 nm.

In the picosecond laser flash photolysis, generation of the absorption bands ascribable to ${}^{\mathrm{T}}C_{76}^{*}$ was observed as shown in Figure 4. The rate constant for the rising absorption−time profile was estimated by fitting to

$$\Delta\mathrm{Abs} = C_4\left(1 - \exp\left(-k_{C_{76}}^{\mathrm{T}} t\right)\right) \quad (4)$$

where C_4 is a constant corresponding to the final absorbance of ${}^{\mathrm{T}}C_{76}^{*}$. In eq 4, it was assumed that the rate constant of generation of ${}^{\mathrm{T}}C_{76}^{*}$ ($k_{C_{76}}^{\mathrm{T}}$) is much larger than its decay rate constant; the first-order decay rate constant of ${}^{\mathrm{T}}C_{76}^{*}$ was estimated to be 1.4×10^5 s^{-1} as mentioned above. In Figure 4, the solid line was obtained assuming $k_{C_{76}}^{\mathrm{T}} = 6.0 \times 10^8$ s^{-1}. Since $k_{C_{76}}^{\mathrm{T}} = (k_{\mathrm{r}}{}^{\mathrm{S}} + k_{\mathrm{nr}}{}^{\mathrm{S}} + k_{\mathrm{isc}})$, where $k_{\mathrm{r}}{}^{\mathrm{S}}$, $k_{\mathrm{nr}}{}^{\mathrm{S}}$, and k_{isc} are radiative and nonradiative rate constants of the singlet excited state and intersystem crossing rate, respectively, the lifetime of the singlet excited state of C_{76} was estimated to be 1.7 ns, which is almost about the same as the reported singlet lifetimes of C_{60} (1.2 ns) and C_{70} (620 ps).[2d,g−i]

Generation of Radical Anion of C_{76} by Electron-Transfer Reaction. It is expected that photoirradiation of the solution containing C_{76} and an appropriate electron donor generates $C_{76}^{\bullet -}$. Using TMPD as an electron donor for electron transfer to ${}^{\mathrm{T}}C_{76}^{*}$, −93 to −54 kJ mol^{-1} of sufficiently negative free energy change is expected from the Rehm−Weller relation[22] employing the triplet energy of C_{76} and oxidation and reduction potentials of TMPD (0.16 V vs SCE)[22] and C_{76} (−0.24 V vs Ag/AgCl)[11a], respectively. Steady-state absorption spectra of benzonitrile solutions containing C_{76} and TMPD were identical to the superpositions of those of C_{76} and TMPD in the examined concentration range (C_{76}, 0.06 mM; TMPD, 2−8 mM). This result indicates that the ground-state complex of C_{76} and TMPD is not formed or can be negligible under the present experimental conditions. Since TMPD does not absorb light at 532 nm, SHG of Nd:YAG laser excites C_{76} only. Since the transient absorption was not observed in the laser photolysis of the benzonitrile solution containing only TMPD with high laser power (ca. 60 mJ/pulse), the multiphoton process of TMPD can be negligible under the present experimental condition. Figure 5 shows the transient absorption spectra of the benzonitrile solution containing C_{76} and TMPD. The transient absorption bands attributed to ${}^{\mathrm{T}}C_{76}^{*}$ decayed within a few hundred nanoseconds. Sharp and broad transient absorption bands appeared at 600 and 880 nm, respectively, after decay of ${}^{\mathrm{T}}C_{76}^{*}$. The former absorption band can be attributed to the radical cation of TMPD (TMPD$^{\bullet +}$).[23] The latter absorption band will be $C_{76}^{\bullet -}$. This identification is supported by the fact that $C_{76}^{\bullet -}$, which was generated by γ irradiation in a frozen MTHF matrix (77 K), showed a similar broad absorption band in the near-IR region (Figure 6).

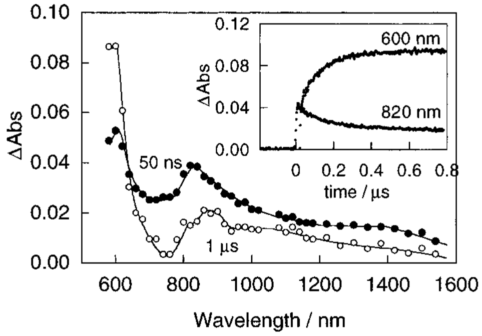

Figure 5. Transient absorption spectra of benzonitrile solution containing 0.06 mM C_{76} and 2 mM TMPD. Excitation is from the SHG of a Nd:YAG laser. The insert shows the absorption−time profiles at 600 and 820 nm.

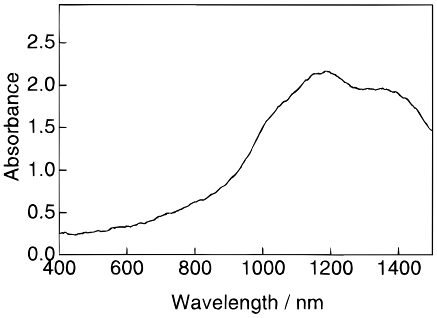

Figure 6. Absorption spectrum of $C_{76}^{\bullet -}$ in MTHF (77 K) generated by γ irradiation.

The transient absorption band around 880 nm in Figure 5 is a superposition of the absorption bands of ${}^{\mathrm{T}}C_{76}^{*}$ and $C_{76}^{\bullet -}$. The absorption−time profile at 820 nm of the solution containing 0.06 mM C_{76} and 2 mM TMPD was well resolved with curves of 8.3×10^6 s^{-1} for the decay rate constant and 8.4×10^6 s^{-1} for the growth rate constant (Figure 7). From the good correspondence of these rate constants and the fact that the laser light at 532 nm excites C_{76} only, it can be reasonably concluded that the radical ions were generated by the electron-transfer reaction from TMPD to ${}^{\mathrm{T}}C_{76}^{*}$, i.e.,

$${}^{\mathrm{T}}C_{76}^{*} + \mathrm{TMPD} \rightarrow C_{76}^{\bullet -} + \mathrm{TMPD}^{\bullet +} \quad (5)$$

From the dependence of the growth rate constant of $C_{76}^{\bullet -}$ ($k_{\mathrm{obs}}^{C_{76}^{\bullet -}}$) on the concentration of TMPD (insert of Figure 7), the bimolecular rate constant of the quenching of ${}^{\mathrm{T}}C_{76}^{*}$ in the present reaction was estimated to be 7.8×10^8 M^{-1} s^{-1}. The reaction rate constants smaller than the diffusion-controlled rate (5.3×10^9 M^{-1} s^{-1} for benzonitrile) have been reported also in fluorescence-quenching reactions between fullerenes (C_{60} and

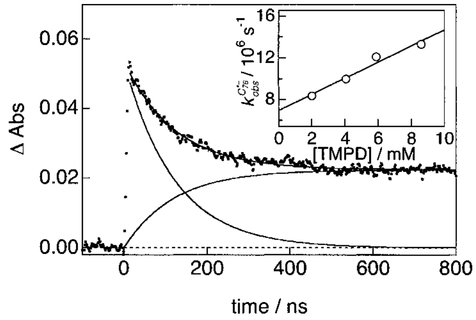

Figure 7. Absorption−time profile at 820 nm observed in the benzonitrile solution containing 0.06 mM C_{76} and 2 mM TMPD excited with SHG of a Nd:YAG laser. Solid lines are fitting curves obtained by assuming the decay of $^{T}C_{76}^{*}$ and the rising of $C_{76}^{\bullet-}$. The insert shows the dependence of $k_{\mathrm{obs}}^{\mathrm{C}_{76}^{\bullet-}}$ on the concentration of TMPD.

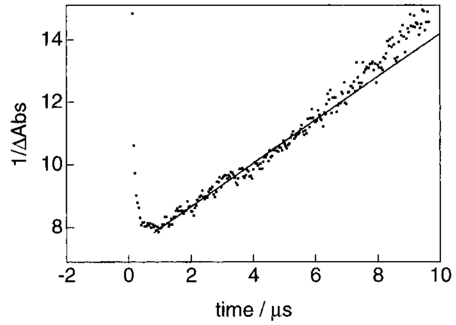

Figure 8. Second-order plot for the decay at 600 nm observed in the benzonitrile solution containing 0.06 mM C_{76} and 2 mM TMPD excited with SHG of a Nd:YAG laser.

C_{70}) and amines such as triethylamine and *N*,*N*-dimethylaniline.[24,25] Furthermore, from the extinction coefficient reported for $TMPD^{\bullet+}$,[23] the extinction coefficient of $C_{76}^{\bullet-}$ at 880 nm was estimated to be 1.5×10^3 M^{-1} cm^{-1}.

The absorption−time profiles of the radical ions show a rise over about 500 ns after laser excitation and then decay. The decay can be attributed mainly to back-electron transfer reaction 6.

$$C_{76}^{\bullet-} + TMPD^{\bullet+} \rightarrow C_{76} + TMPD \qquad (6)$$

Second-order plot of the absorption−time profile at 600 nm corresponding to $TMPD^{\bullet+}$ is shown in Figure 8. From the slope of the plot, the back-electron transfer rate (k_{bet}) was estimated to be 2.8×10^9 M^{-1} s^{-1} employing an extinction coefficient of $TMPD^{\bullet+}$ at 600 nm of 5.9×10^3 M^{-1} cm^{-1}.[23] The result indicates that the generated radical ions decay by the back-electron transfer reaction at a rate close to the diffusion limit. Slight deviation from the fitted line at the later part suggests the existence of the other decay pathway in addition to the back-electron transfer reaction.

After several hundred laser shots, the absorption spectrum of the solution containing both C_{76} and TMPD shows new absorption bands at 620, 560, and 429 nm (Figure 9). The former two absorption bands can be attributed to $TMPD^{\bullet+}$, which is known to be very stable in its radical cation form. The identification of the absorption band at 429 nm is uncertain at the present stage of our study. In the case of C_{60} and aliphatic amines, it was reported that photoirradiation generates stable addition products including macromolecules.[25] Therefore, a similar stable product is expected as a possible origin of the absorption band at 429 nm.

Conclusion

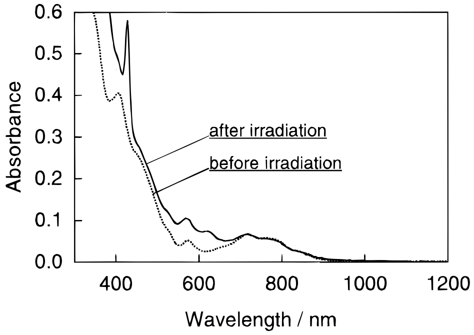

Figure 9. Absorption spectra of the benzonitrile solution containing 0.06 mM C_{76} and 2 mM TMPD before and after several hundred laser excitations (SHG of Nd:YAG laser).

The transient absorption spectrum of $^{T}C_{76}^{*}$ and its generation and decay profiles were observed in the nano- and picosecond laser flash photolysis in the visible and near-IR regions. In the presence of *β*-carotene in toluene, $^{T}C_{76}^{*}$ was deactivated by the energy-transfer reaction. The extinction coefficient of $^{T}C_{76}^{*}$ was also estimated from the transient absorption spectra. Photoinduced electron-transfer reaction between $^{T}C_{76}^{*}$ and TMPD was confirmed, and its bimolecular rate constant was estimated to be 7.8×10^8 M^{-1} s^{-1}. The generated radical ions decayed by the back-electron transfer at a rate close to the diffusion limit. These results indicate that C_{76} behaves as an electron acceptor in photochemical reactions as C_{60} and C_{70}.

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