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Triplet Properties and Photoinduced Electron-Transfer Reactions of C_{120}, the [2+2] Dimer of Fullerene C_{60}

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Photophysical and photochemical properties of a [2+2] fullerene dimer, C_{120}, have been characterized by laser flash photolysis. By laser irradiation to C_{120}, a triplet−triplet absorption band appeared at 700 nm. From triplet energy-transfer reactions with some energy acceptors, photophysical properties of C_{120}, including triplet energy, extinction coefficient, and quantum yield of the intersystem crossing process, were estimated. Reduction of C_{120} in the ground state by tetrakis(dimethylamino)ethylene resulted in decomposition into $C_{60}^{\bullet -}$ and C_{60}. Photoinduced electron transfer from *N,N,N′,N′*-tetramethyl-1,4-phenylenediamine to triplet-excited C_{120} was confirmed by the observation of a transient absorption band due to the radical anion of C_{120} at 1020 nm. Electron-transfer rates between triplet-excited C_{120} and various electron-donors were explained by the semiempirical Rehm−Weller relation. Oxidation of triplet-excited C_{120} was also observed by employing tetracyanoethylene as an electron-acceptor.

Introduction

A great deal of attention have been paid to fullerene polymers and oligomers that have been prepared by photopolymerization, etc.[1−4] Recently, several synthetic methods for preparation of covalent bond between fullerenes have been developed to form well-structured fullerene oligomers. Bulk synthesis of C_{120}, which includes two C−C bonds between two C_{60} cages (Figure 1), was achieved by solid-state mechanochemical reaction of C_{60} with KCN.[5] $C_{120}O$ and $C_{121}H_2$, which involve a C−O−C or a C−CH_2−C bond between fullerenes as well as a C−C bond, have been reported to be synthesized by a thermal reaction of C_{60} and $C_{60}O$ or $C_{61}H_2$, respectively.[6] It has been confirmed that the reaction of $C_{60}O$ and C_{70} gives $C_{130}O$, a heterodimer, by a similar thermal reaction.[7] A tetralinked fullerene dimer, $C_{120}O_2$, was also reported to be obtained as a byproduct of the reaction of the solid mixture of $C_{60}O$ with C_{60}.[8] Heterofullerenes $C_{59}N^{\bullet}$ and $C_{69}N^{\bullet}$, neutral radicals, were isolated as dimers $(C_{59}N)_2$ or $(C_{69}N)_2$, respectively.[9]

Fullerene dimers, especially C_{120}, can be considered to be the smallest subunit of the 1-dimensional fullerene polymers.[5b] Therefore, investigation of the properties of fullerene dimers seems to be important to elucidate properties of 1- and 2-dimensional fullerene polymeric materials. From this viewpoint, several experimental and theoretical investigations have been reported.[10,11]

Very recently, Sun et al.[12] reported fluorescence and triplet properties of C_{120} as well as those of a fullerene polymer. They also reported quenching of C_{120} fluorescence by dimethylaniline, but the generation of the radical anion of C_{120} was not confirmed directly by a spectroscopic method.

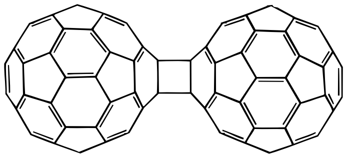

Figure 1. Molecular structure of C_{120}.

In the present paper, we reported results of nanosecond and picosecond laser flash photolysis studies of C_{120}. From the transient absorption spectra both in the visible and near-infrared regions, triplet properties, including triplet energy, extinction coefficient of a triplet−triplet absorption band, and quantum yield of the intersystem crossing process, were evaluated. These properties were not evaluated in the previous study.[12] Photoinduced electron-transfer reactions between C_{120} and electron-donors were also confirmed by observing the absorption band due to the radical anion of C_{120}. The oxidation reaction of C_{120} in the triplet excited state was also confirmed. These spectroscopic and rate data were compared with those of C_{60} and C_{60} derivatives.

Experimental Section

Materials. C_{120} was prepared by mechanochemical KCN catalyzed [2+2] cycloaddition of C_{60} as reported in previous papers.[5]

N,N,N′,N′-Tetramethyl-1,4-phenylenediamine (TMPD) was prepared from *N,N,N′,N′*-tetramethyl-1,4-phenylenediamine dihydrochloride (Kanto Chemicals) by neutralization with NaOH just before use. Tetracyanoethylene (TCNE) was purchased from

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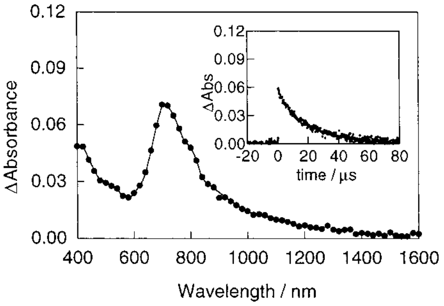


Figure 2. Transient absorption spectrum of C_{120} (3.5×10^{-5} M) in DCB at 100 ns after the 355-nm laser irradiation. Insert: Absorption−time profile at 700 nm.

Nacalai Tesque and purified by recrystallization from CH_2Cl_2. Other chemicals were of the best commercial grade available. In the present study, *o*-dichlorobenzene (DCB) was used as a solvent for all spectroscopic measurements because of the appreciable solubility of C_{120}. To avoid degradation, all sample solutions were prepared just before the measurements.

Spectroscopic Measurements. Transient absorption spectra in the near-IR region (600−1600 nm) were measured using the second-harmonic generation (SHG, 532 nm) or third-harmonic generation (THG, 355 nm) of an Nd:YAG laser (Spectra-Physics, Quanta-Ray GCR-130, 6 ns fwhm) as an excitation source. Monitoring light from a pulsed Xe-lamp was detected with a Ge avalanche photodiode (APD) (Hamamatsu Photonics, B2834). For spectra in the visible region (400−1000 nm), an Si-PIN photodiode (Hamamatsu Photonics, S1722−02) was used as the detector. Triplet lifetime was estimated with a photomultiplier. Details of the transient absorption measurements were described in our previous reports.[13] All the samples in a quartz cell (1 × 1 cm) were deaerated by bubbling Ar through the solution for 15 min.

Transient absorption spectra in the ps-region were estimated by using the THG (355 nm) of an active/passive mode-locked Nd:YAG laser (Continuum, PY61C-10, 30 ps fwhm) as an excitation source. Probe light that was generated by breakdown of Xe gas was detected with a streak scope (Hamamatsu Photonics, C2830) equipped with a polychromator (Acton Research Corp., SpectraPro-150) and a cooled charge-coupled device (CCD) camera (Hamamatsu Photonics, C4880) after passing through the sample solution.

Steady-state absorption spectra in the visible and near-IR regions were measured with a JASCO V-570DS spectrometer at room temperature.

Electrochemical Measurements. Cyclic voltammetry was carried out with a potentiostat (Hokuto Denko, HAB-151) in a conventional three-electrode cell equipped with Pt working and counter electrodes and an Ag/AgCl reference electrode at room temperature. Sample solution was deaerated by Ar bubbling.

Results and Discussion

Characterization of Triplet State of C_{120}. The 355 nm-laser irradiation to C_{120} in DCB generated transient absorption bands at 700 and <400 nm accompanying a shoulder around 540 nm and an absorption tail to ~1400 nm (Figure 2). The absorption bands can be attributed to a triplet excited state of C_{120} ($^3C_{120}{}^*$) because the absorption bands were quenched in the presence of oxygen, a triplet energy quencher, at a rate of 1.2×10^9 $M^{-1}s^{-1}$. In deaerated solution, the decay rate of the absorption band was estimated to be 4.4×10^4 s^{-1}, which corresponds to 23 μs of triplet lifetime. The estimated lifetime was somewhat longer than that previously estimated by Sun et al.,[12] but rather similar to triplet lifetimes of 1,2-adducts of C_{60} (20−70 μs).[14] Therefore, the spectroscopic features of $^3C_{120}{}^*$, including peak position and lifetime, were close to those of 1,2-adducts of C_{60}.

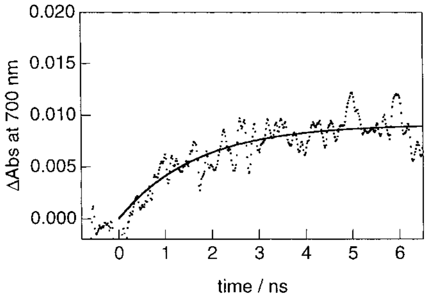


Figure 3. Absorption−time profile of C_{120} in DCB at 700 nm.

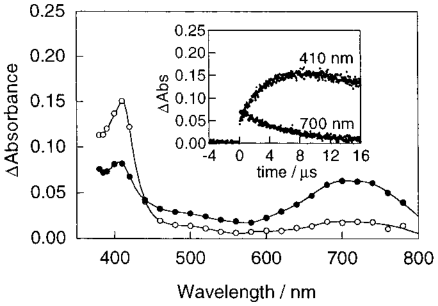


Figure 4. Transient absorption spectra of C_{120} (4×10^{-5} M) and *trans*-retinol (8.6×10^{-4} M) in DCB at 1 and 10 μs (filled and open circles, respectively) after the 532-nm laser irradiation. Insert: Absorption−time profiles at 700 and 410 nm.

It has been reported that C_{120} in solution decomposes by room light at the rate of 2% per day.[5b] In our experiments, however, a steady-state absorption band due to the product of decomposition was not confirmed after the laser irradiation of the sample solutions, indicating a negligible effect of decomposition on our experimental results.

By using the ps-laser flash photolysis system, generation of the triplet absorption band was observed at 700 nm (Figure 3). The absorption−time profile was fitted well with the first-order rise function as shown by the solid line in Figure 3. The rate constant for the rising absorption−time profile was estimated to be 6.1×10^8 s^{-1}, which corresponds to 1.6 ns of singlet lifetime. The estimated singlet lifetime was in good agreement with the value estimated from a fluorescence decay profile obtained by Sun et al.[12]

The absorption band of $^3C_{120}{}^*$ was quenched efficiently by *trans*-retinol as well as by oxygen. In transient absorption spectra recorded following the 355-nm laser irradiation of a solution containing C_{120} and retinol (Figure 4), an absorption band at 410 nm due to triplet-excited retinol was generated with a decrease of $^3C_{120}{}^*$. This finding can be attributed to the triplet energy transfer from $^3C_{120}{}^*$ to retinol (eq 1), the triplet energy (E_T) of which was reported to be 1.45 eV.[15]

$$C_{120} \xrightarrow{hn\ (355\ \mathrm{nm})} {}^1C_{120}{}^* \xrightarrow{isc.} {}^3C_{120}{}^* \xrightarrow[+\mathrm{retinol}]{k_{\mathrm{ent}}} C_{120} + {}^3(\mathrm{retinol})^* \quad (1)$$

From a relation between the concentration of retinol and the decay rate of $^3C_{120}{}^*$, a bimolecular reaction rate for the present energy-transfer reaction (k_{ent}) was estimated to be 4.5×10^9 M^{-1} s^{-1}, which is close to the value of the diffusion-limiting rate of DCB ($k_{diff} = 5.0 \times 10^9$ M^{-1} s^{-1}). This finding indicates the efficient energy transfer from $^3C_{120}{}^*$ to retinol.

TABLE 1: Reaction Rate Constants (k_{ent}) of Energy Transfer Reactions from $^3C_{120}$*

triplet energy acceptor	E_T of energy acceptor, eV	k_{ent}, $M^{-1}\ s^{-1}$[a]
β-carotene	0.91	4.3×10^9[b]
oxygen	0.98	1.2×10^9[c]
tetracene	1.27	2.0×10^9
trans-retinol	1.45	4.5×10^9
C_{60}	1.56	$<10^8$
anthracene	1.84	n. r.[d]

[a] In DCB. [b] Reaction rate was estimated by multiplying the quantum yield to the triplet quenching rate (see text). [c] Reaction rate was estimated from oxygen concentration reported for chlorobenzene.[15] [d] No reaction.

TABLE 2: Photophysical Properties of Fullerenes in Excited States

property	C_{60}[a]	$C_{60}R$[a,b]	C_{120}[c]
singlet			
singlet energy, eV	1.7	1.7−1.8	1.7[d]
lifetime, ns	1.2	1.2−1.3	1.6
Φ_F	3.2×10^{-4}	$1.0-1.2 \times 10^{-3}$	7.9×10^{-4}[d]
triplet			
$T-T$ absorption, nm	400, 740	680−700	<400, 700
ϵ_T, $M^{-1}\ cm^{-1}$	1.6×10^4	$1.4-1.6 \times 10^4$	1.4×10^4
E_T, eV	1.56	1.50	~1.5
τ_T, μs	55	24−29	23
Φ_{isc}	1.0	0.88−0.95	0.7 ± 0.1

[a] In toluene. [b] From ref 14d. [c] In DCB. [d] From ref 12.

A similar triplet energy-transfer reaction was also confirmed by using tetracene as a triplet energy acceptor. The reaction rates as well as the E_T of the energy acceptors are summarized in Table 1 . On the other hand, the triplet energy-transfer reaction was not observed when the laser was irradiated to C_{120} in the presence of anthracene. This finding resulted from the higher triplet energy of anthracene ($E_T = 1.85$ eV) than that of $^3C_{120}$*.[15] Furthermore, when C_{60} was employed as an energy acceptor ($E_T = 1.56$ eV), appreciable energy transfer was not observed. Therefore, the triplet energy of $^3C_{120}$* is considered to be ~1.5 eV.

The extinction coefficient (ϵ_T) of $^3C_{120}$* at 700 nm was estimated to be $1.4 \times 10^4\ M^{-1}\ cm^{-1}$ from the comparison with the generated triplet absorption band of energy acceptors (tetracene and β-carotene). Furthermore, the quantum yield of the intersystem crossing process (Φ_{isc}) of C_{120} was estimated to be 0.7 ± 0.1 by the relative actinometry method using the triplet absorption band of anthracene as a standard ($\epsilon_T = 4.55 \times 10^4\ M^{-1}\ cm^{-1}$ and $\Phi_{isc} = 0.71$).[15,16] The estimated ϵ_T value is close to the reported values for C_{60} and 1,2-adducts of C_{60} (Table 2).[14,17] On the other hand, Φ_{isc} is somewhat smaller than that of C_{60}.[17,18] Because a small Φ_{isc} is also reported for 1,2-adducts of C_{60},[14] it can be concluded that the reduction of symmetry of the fullerene moiety causes a decrease in Φ_{isc} as well as an increase in fluorescence quantum yields (Φ_F). Singlet and triplet properties of C_{120}, as well as those of C_{60} and 1,2-adducts of C_{60}, are summarized in Table 2.

From the comparison of the ground-state absorption spectrum of C_{120} with those of C_{60} and 1,2-adducts of C_{60}, Sun et al. indicated that two cages in the C_{60} dimer are independent without substantial interactions with respect to electronic transition.[12] They also indicated that the photoexcitation is likely localized at one of the two fullerene cages in the C_{60} dimer. As for the triplet excited state for the C_{60} dimer, the estimated triplet parameters are close to those of 1,2-adducts of C_{60}, indicating that the triplet excited state also seems to be localized on one fullerene-cage without substantial interaction among two fullerene cages.

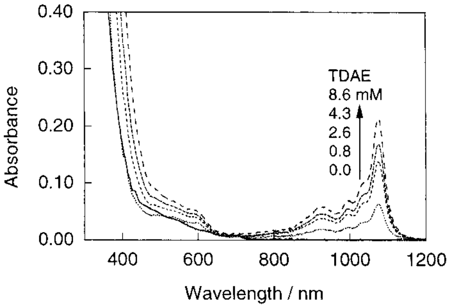


Figure 5. Absorption spectra of C_{120} (7.9×10^{-6} M) in the absence and presence of TDAE in benzonitrile. Concentrations of TDAE are indicated by numbers close to spectra.

Ground-State Reduction of C_{120}. Fullerenes are good electron-acceptors both in the excited and ground states. Recently, we reported that, in the presence of tetrakis(dimethylamino)ethylene (TDAE), fullerenes are in equilibrium with the corresponding radical ions in appropriate polar solvents.[19] By adding TDAE to C_{120} in DCB, a new absorption band appeared at 1076 nm (Figure 5). The new absorption band can be attributed to the radical anion of C_{60} ($C_{60}^{\bullet -}$), because the peak position corresponds well with the reported one.[19,20] Absorbance of $C_{60}^{\bullet -}$ increased as the amount of TDAE increased. These findings indicate that the reduced C_{120} is ready to decompose into C_{60} and $C_{60}^{\bullet -}$, which are in equilibrium as show in eqs 2 and 3:

$$C_{120} + TDAE \rightleftharpoons (C_{120}^{\bullet -}) + TDAE^{\bullet +} \rightarrow C_{60}^{\bullet -} + C_{60} \qquad (2)$$

$$C_{60} + TDAE \overset{K}{\rightleftharpoons} C_{60}^{\bullet -} + TDAE^{\bullet +} \qquad (3)$$

where K is an equilibrium constant. Because the spectral shape was not changed with an increase in the concentration of TDAE, decomposition of $C_{120}^{\bullet -}$ seems to proceed immediately after reduction by TDAE. The decomposition of $C_{120}^{\bullet -}$ into $C_{60}^{\bullet -}$ and C_{60} has also been confirmed in electrochemical study reported previously.[5b] By applying the procedure reported in the previous report,[19] the K value was estimated to be 0.011, which is close to the value estimated for the equilibrium among C_{60}, TDAE, and corresponding radical ions in DCB.

Reduction of C_{120} in the Triplet State. Because the reduction potential and triplet energy of C_{120} are close to those of C_{60},[5b] C_{120} is also expected to be a good electron-acceptor in the triplet excited state. At 100 ns after the 532 nm-laser irradiation of a solution containing C_{120} and TMPD, the absorption band due to $^3C_{120}$* appeared at 700 nm (Figure 6), because the 532 nm-laser excited only C_{120}. At 1 μs after the laser irradiation, the absorption band due to $^3C_{120}$* was quenched and absorption bands at 1020, 640, and 580 nm were confirmed. The latter two absorption bands can be attributed to the radical cation of TMPD.[21] The absorption band at 1020 nm can be assigned to the radical anion of C_{120} ($C_{120}^{\bullet -}$) because the absorption band corresponds well with those observed with radical anions of 1,2-adducts of C_{60}.[14] Because the triplet decay rate of C_{120} was accelerated in the presence of TMPD, the electron-transfer reaction is considered to proceed via the triplet excited state of C_{120} (eq 4)

$$^3C_{120}^{*} + TMPD \xrightarrow{k_{et}} C_{120}^{\bullet -} + TMPD^{\bullet +} \qquad (4)$$

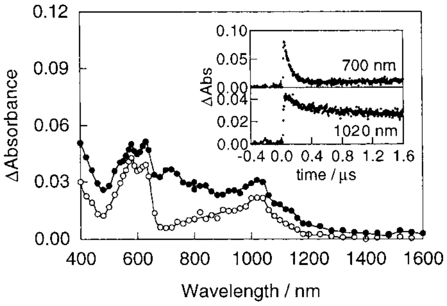


Figure 6. Transient absorption spectra of C_{120} (4×10^{-5} M) and TMPD (2.4×10^{-3} M) in DCB at 100 ns and 1 μs (filled and open circles, respectively) after the 532-nm laser irradiation. Insert: Absorption−time profiles at 1020 and 700 nm.

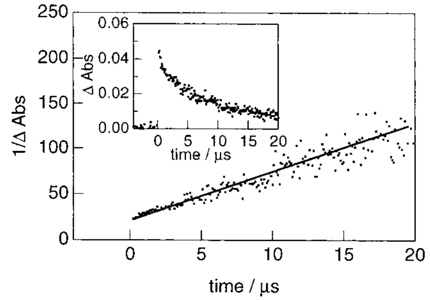
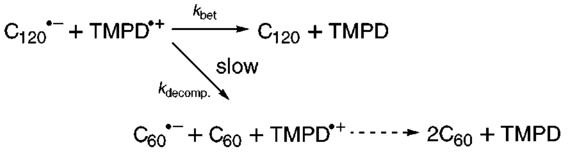


Figure 7. Second-order plot of absorption−time profile at 700 nm of C_{120} and TMPD (see Figure 6). Insert: Absorption−time profile at 700 nm.

From the relation between the decay rate of ${}^3C_{120}{}^*$ and the concentration of TMPD, the bimolecular reaction rate ($k_q{}^T$) was estimated to be 5.3×10^9 $M^{-1}s^{-1}$, indicating a diffusion-controlled process. Furthermore, from the comparison with the absorption band of $TMPD^{\bullet+}$, the extinction coefficient of $C_{120}{}^{\bullet-}$ was estimated to be 3.5×10^3 $M^{-1}cm^{-1}$ at 1020 nm. The estimated value is much smaller than that of $C_{60}{}^{\bullet-}$ but similar to those of 1,2-adducts of C_{60}.[22,14] The similarity of the absorption spectrum of $C_{120}{}^{\bullet-}$ to those of the 1,2-adducts of C_{60} suggests that interaction among fullerene cages is also negligibly small in the radical ion state. For a radical ion of a component molecule interacting with a corresponding neutral component molecule located at a very close position, the appearance of new absorption band in the longer wavelength region would be expected, as in the case of the charge resonance band of poly(*N*-vinylcarbazole),[23] but $C_{120}{}^{\bullet-}$ does not show such an absorption band. This finding indicates that a minus charge of $C_{120}{}^{\bullet-}$ is also localized on one fullerene-cage of the dimer molecule, as in the case of excited states.

The absorption−time profile of the radical ion shows decay over several 10-μs periods, as shown in the insert of Figure 7. The decay of the radical ions can be attributed to the back-electron-transfer reaction (eq 5) because the steady-state absorption spectrum of the sample solution was not changed after the laser irradiation. This finding indicates that the decomposition of $C_{120}{}^{\bullet-}$ into $C_{60}{}^{\bullet-}$ and C_{60} was a slower reaction than the back-electron-transfer reaction between $C_{120}{}^{\bullet-}$ and $TMPD^{\bullet+}$.



(5)

By applying a second-order plot, the back-electron-transfer rate (k_{bet}) was estimated to be 3×10^{10} M^{-1} s^{-1}, which is a diffusion-limiting process. Therefore, the rate for the decomposition ($k_{decomp.}$) should be slower than the order of 10^5 s^{-1}.

TABLE 3: The $k_q{}^T$ Values of the Electron Transfer Reactions of C_{60}, $C_{60}R$, and C_{120} in DCB

triplet quencher	$E_{1/2}$,[a] V versus Ag/AgCl[a]	$k_q{}^T$, M^{-1} s^{-1}[b] C_{60}	$C_{60}R$[c]	C_{120}
electron donor				
TMPD	0.42	6.4×10^9	4.7×10^9	5.3×10^9
TMB[d]	0.63	5.6×10^9	3.7×10^9	4.9×10^9
DABCO	0.85	1.6×10^9	1.4×10^8	8.6×10^8
N,*N*-diethylaniline	0.98	1.7×10^8	1.1×10^5	3.0×10^6
N,*N*-dimethylaniline	0.99	3.5×10^7	3.6×10^4	7.4×10^5
electron acceptor				
TCNE	0.41	1.3×10^9	3.3×10^9	1.2×10^9

[a] Oxidation ($E(D^{\bullet+}/D)$) and reduction ($E(A/A^{\bullet-})$) potentials were estimated in DCB containing 5 mM of donor or acceptor and 50 mM of Bu_4NBF_4; scan rate was 20 mV/s. [b] In DCB. [c] $C_{60}(C_3H_6N)pC_6H_4CHO$. [d] *N*,*N*,*N*′,*N*′-Tetramethylbenzidine.

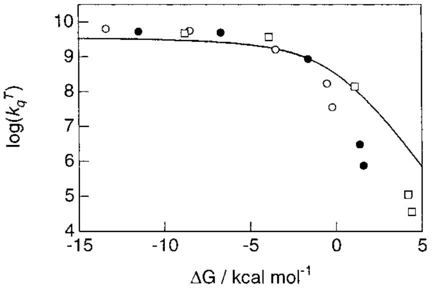


Figure 8. Relation between $k_q{}^T$ values and ΔG for the electron-transfer reactions of C_{120} (filled circle), C_{60} (open circle), and $C_{60}(C_3H_6N)pC_6H_4$-CHO (open square). The solid line was calculated from the Rehm−Weller equation.[24]

Similar electron-transfer reactions were also confirmed with various electron-donors. Electron-transfer rates between C_{120} and electron-donors, as well as those of C_{60} and a 1,2-adduct of C_{60} ($C_{60}R$, $C_{60}(C_3H_6N)pC_6H_4CHO$), are summarized in Table 3. Because the reduction potential of $C_{60}R$ (−0.91 V versus Ag/AgCl)[24] is cathodic compared with those of C_{120} (−0.77) and C_{60} (−0.79), the reaction rates of $C_{60}R$ are slower than those of C_{120} and C_{60} for all electron-donors. Furthermore, the electron-transfer rates of fullerenes decreased as oxidation potentials of electron-donors increased. The oxidation potentials of donors in the present study are also summarized in Table 3. These findings can be explained on the basis of free energy change for the electron-transfer reaction. In Figure 8, observed $k_q{}^T$ values were plotted against the free energy changes (ΔG) calculated by assuming the encounter distance of radical ions and the triplet energy of C_{120} are to be 7 Å and 1.50 eV, respectively.[25] The relationship between ΔG and the electron-transfer rate calculated from the Rehm−Weller equation[25] was also plotted as a solid line (Figure 8), which shows a rather good fit with the experimental results. A slight deviation between the solid line and the experimental data would result from underestimation of encounter distance of radical ions. For electron-transfer reactions between small molecules, 7 Å is often employed as an encounter distance,[25,26] whereas fullerenes have larger sizes than common molecules. Because an increase in encounter distance results in an increase in ΔG, the experimental data in Figure 8 need to shift slightly in a positive direction on the ΔG axis.

β-Carotene is known as a good triplet energy acceptor; its triplet energy is as low as 0.91 eV.[15] In transient absorption spectra of β-carotene and C_{120}, triplet energy transfer was confirmed by observing generation of a triplet absorption band

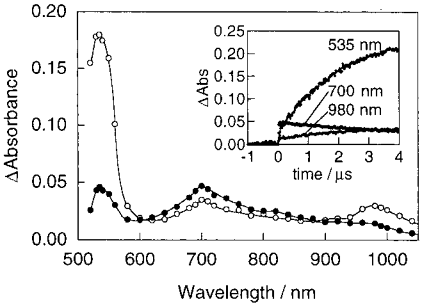
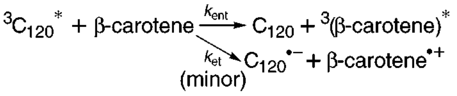


Figure 9. Transient absorption spectra of C_{120} (4 × 10^{-5} M) and *β*-carotene (9 × 10^{-5} M) in DCB at 250 ns and 2.5 *μ*s (filled and open circles, respectively) after the 355-nm laser irradiation. Insert: Absorption−time profiles at 980, 700, and 535 nm.

of *β*-carotene at 535 nm with a decrease of $^3C_{120}{}^*$ (Figure 9 and insert). Furthermore, electron transfer-reaction is also confirmed in the present reaction mixture. The new absorption band that appeared at 980 nm can be attributed to the radical cation of *β*-carotene, predominantly, because an extinction coefficient of the radical cation of *β*-carotene (1.0 × 10^5 M^{-1} cm^{-1})[27] is much larger than that of $C_{120}{}^{\bullet -}$. In our previous paper, we confirmed that *β*-carotene acts as an electron-donor to $^3C_{60}{}^*$ in polar solvents such as benzonitrile (dielectric constant: $\epsilon_s = 25.2$),[15] whereas only triplet energy transfer occurred in a nonpolar solvent.[28] In the present case, because DCB is moderatory polar solvent ($\epsilon_s = 9.93$),[15] an energy transfer reaction is the predominant process. Quantum yields for the electron and energy transfer reactions are estimated to be 0.18 and 0.82, respectively, using reported extinction coefficients. Because k_q^T value was 5.2 × 10^9 M^{-1} s^{-1}, electron (k_{et}) and energy transfer reaction rates (k_{ent}) were evaluated to be 0.9 × 10^9 and 4.3 × 10^9 M^{-1} s^{-1}, respectively (eq 7)


$$^3C_{120}{}^* + \beta\text{-carotene} \xrightarrow{k_{ent}} C_{120} + {}^3(\beta\text{-carotene})^* \qquad \xrightarrow{k_{et}} \underset{\text{(minor)}}{} C_{120}{}^{\bullet -} + \beta\text{-carotene}^{\bullet +} \tag{7}$$

Oxidation of C_{120} in Triplet State. It has been reported that the oxidation reaction of fullerenes in the triplet excited state also proceeds using a strong electron-acceptor such as TCNE.[29] Here, the oxidation of C_{120} via photoinduced electron-transfer reaction was attempted employing TCNE as an acceptor. Figure 10 shows transient absorption spectra obtained by the 355 nm-laser irradiation of a DCB solution containing C_{120} and TCNE. Although $^3C_{120}{}^*$ was confirmed at 100 ns after the laser irradiation, new absorption bands appeared at 1160, 920, and <460 nm in the spectrum at 1 *μ*s after decaying $^3C_{120}{}^*$. The absorption band at <460 nm can be attributed to the radical anion of TCNE,[30] whereas the absorption bands at 1160 and 920 nm are assigned to the radical cation of C_{120}. Radical cations of 1,2-adducts of C_{60} show absorption bands around 1120 and 880 nm.[31] These findings indicate the radical cation formation by electron-transfer reaction from $^3C_{120}{}^*$ to TCNE as eq 8

$$^3C_{120}{}^* + \text{TCNE} \rightarrow C_{120}{}^{\bullet +} + \text{TCNE}^{\bullet -} \tag{8}$$

The reaction rate was estimated to be 1.2 × 10^9 M^{-1} s^{-1}, which is a similar value to that of C_{60} but slower than that for 1,2-adducts of C_{60} (Table 3). This finding can be attributed to lower electron-donor abilities of C_{120} and C_{60} in triplet states than 1,2-adducts of C_{60}.

Summary

Characteristics of $^3C_{120}{}^*$ were evaluated by the laser flash photolysis method. The estimated parameters of $^3C_{120}{}^*$ were quite similar to those of 1,2-adducts of C_{60}, indicating a localized triplet excited state as well as in the ground and singlet excited states. Reduced C_{120} is unstable to decompose to $C_{60}{}^{\bullet -}$ and C_{60}, but the absorption spectrum of $C_{120}{}^{\bullet -}$ was successfully observed in photoinduced electron transfer reaction in the excited state. The fast back-electron-transfer reaction effectively prevented decomposition. The oxidation reaction of C_{120} was also confirmed by laser flash photolysis. Observed absorption spectra of the radical anion and cation of C_{120} are close to those of 1,2-adducts of C_{60}, indicating negligible interactions both in the reduced and oxidized forms. The reactivity of excited C_{120} was explained well by the Rehm−Weller equation, as in the cases of C_{60} and a 1,2-adduct of C_{60}.

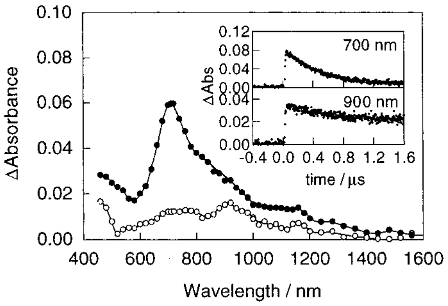


Figure 10. Transient absorption spectra of C_{120} (4 × 10^{-5} M) and TCNE (1.8 × 10^{-3} M) in DCB at 100 ns and 1 *μ*s (filled and open circles, respectively) after the 532-nm laser irradiation. Insert: Absorption−time profiles at 900 and 700 nm.

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