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Photophysical and Photochemical Properties of $C_{120}O$, a C_{60} Dimer Linked by a Saturated Furan Ring

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Photophysical and photochemical properties of $C_{120}O$, a C_{60} dimer linked by a saturated furan ring, have been characterized by various time-resolved spectroscopic methods. A steady-state absorption band of $C_{120}O$ is blue-shifted compared with those of 1,2-adducts of C_{60} ($C_{60}R$). The fluorescence lifetime and quantum yield were estimated to be 1.7 ns and 8.7×10^{-4}, respectively, which are similar to those of $C_{60}R$ and C_{120}. On the other hand, the lifetime of the triplet excited state ($^3C_{120}O^*$) was estimated to be 0.16 μs, which is quite shorter than those of C_{60} (55 μs), $C_{60}R$ (24−29 μs), and C_{120} (23 μs). Furthermore, the quantum yield for the intersystem crossing process was as low as 0.48. These unusual triplet properties of $^3C_{120}O^*$ indicate that the triplet excited C_{60} moiety in $^3C_{120}O^*$ was influenced by an adjacent π-electron system of another C_{60} moiety in the ground state. Ground-state reduction of $C_{120}O$ was observed in the reaction with tetrakis(dimethylamino)ethylene, indicating the stable radical anion formation of $C_{120}O$, in contrast to the unstable radical anion of C_{120}. Photoinduced electron transfer from 1,4-diazabicyclo[2.2.2]octane to $^3C_{120}O^*$ was confirmed by an observation of the transient absorption band of the radical anion of $C_{120}O$ in the near-IR region. Oxidation of $C_{120}O$ was also performed by employing a cosensitization method. The reaction rate constants of the both photoinduced reduction and oxidation were slightly smaller than those of C_{60} and $C_{60}R$.

Introduction

Fullerenes are chemically active molecules. Many derivatives have been synthesized by various methods including photochemical syntheses.[1] Fullerenes are also reactive to the fullerenes themselves. It has been demonstrated that C_{60} forms all-carbon oligomers and polymers under the several conditions.[2−5] Fullerene dimer is the smallest unit including fullerene−fullerene bonds and will be of importance to elucidate properties of 1-dimensional and 2-dimensional fullerene polymeric materials.[6] $C_{120}O$ (Figure 1), which linked two C_{60} molecules by a saturated furan ring, has been reported to be synthesized by a thermal reaction of $C_{60}O$ and C_{60}.[7] $C_{120}O$ is known as a precursor to give C_{119} which is expected to be a peanut-shaped fullerene.[8] It has been confirmed that the reaction of $C_{60}O$ and C_{70} gives $C_{130}O$, heterodimer, by the same manner.[9] A tetra-linked 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}.[10]

Investigations on dimer molecules have made clear many critical and valuable aspects of various kinds of polymeric materials and molecular assemblies: For example, special pair of photosynthetic center and its mimic systems have been widely investigated by many groups.[11] On the fullerene dimers, however, only a few studies are reported elucidating their properties, while interesting properties are expected from their extended π-structures. In the case of $C_{120}O$, electrochemistry,[12] EPR,[12] and Raman spectroscopy[9,13] as well as theoretical studies[14] have been reported in order to examine its properties. The electrochemical study revealed reduction processes which generate the anions, $C_{120}O^{n-}$, where $n = 1-6$.[12] Since fullerenes act as good electron acceptors in their excited states,[15] $C_{120}O$ is also expected to behave similarly. The electron-transfer process is very important in order to understand various functions of materials as well as an initial step in the several synthetic mechanisms.

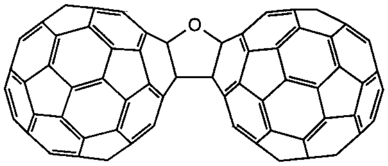

Figure 1. Molecular structure of $C_{120}O$.

As for the photophysical and photochemical properties of fullerene dimer, C_{120} was investigated by two groups.[16,17] Its triplet properties and photoinduced reactivities were quite similar to those of 1,2-adducts of C_{60} ($C_{60}R$), indicating localized nature of the triplet and radical ion states in a C_{60} moiety. Compared to C_{120}, the π-electrons of the C_{60} moieties of $C_{120}O$ locate at a close position due to its bent structure. In the present paper, we investigated the photophysical and photochemical properties of $C_{120}O$. It was revealed that the triplet properties of $C_{120}O$ were much different from those of C_{60}, $C_{60}R$, and C_{120}.

Experimental Section

Materials. $C_{120}O$ was isolated from fullerene soot by hydrothermally initiated dynamic extraction.[18] Purity of the

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sample was >99%. Tetrakis(dimethylamino)ethylene (TDAE), biphenyl (BP), and 1,4-diazabicyclo[2.2.2]octane (DABCO) were purchased from Aldrich and Kanto Chemicals and used as received. Tetracyanoethylene (TCNE) was purchased from Nacalai Tesque and purified by recrystallization from dichloromethane several times. *N*-Methylacridinium hexafluorophosphate (NMA^+) was synthesized by the procedure reported by Gebert et al.[19] Solvents for the measurements were of the best grades available commercially.

Apparatus. Steady-state fluorescence spectra of the sample were measured on a Shimadzu RF-5300PC spectrofluorophotometer. Luminescence spectra in the near-IR region were measured by using an argon ion laser (Spectra-Physics, Beam-Lok 2060-10-SA, 488 nm, ca. 200 mW) as an excitation source. The emission from the sample was focused on to a monochromator (Koken Kogyo, SG-100) equipped with an InGaAs−PIN photodiode (New Focus, 2153). The output signal was recorded using a lock-in amplifier (NF Electronic Instruments, LI 5640).

Fluorescence lifetimes were measured by a single-photon-counting method using an argon ion laser, a pumped Ti:sapphire laser (Spectra-Physics, Tsunami 3950-L2S, fwhm 1.5 ps) with a pulse selector (Spectra-Physics, 3980), a second harmonic generator (Spectra-Physics, GWU-23PS), and a streakscope (Hamamatsu Photonics, C4334−01). In the present study, the sample was excited with 400 nm laser.[20]

Transient absorption spectra in the picosecond region were measured by using second harmonic generation (SHG, 532 nm) of an active/passive mode-locked Nd:YAG laser (Continuum, PY61C-10, 35 ps fwhm) as an excitation source. A probe light which was generated by breakdown of Xe gas was detected with a streak scope (Hamamatsu Photonics, C2830) equipped with a polychromator and a cooled CCD camera (Hamamatsu Photonics, C4880) after passing through the sample solution.[17]

The nanosecond time-resolved absorption spectra were measured using SHG (532 nm) or third harmonic generation (THG, 355 nm) of a Nd:YAG laser (Spectra-Physics, Quanta-Ray GCR-130, fwhm 6 ns) as an excitation source. A pulsed xenon flash lamp (Tokyo Instruments, XF80−60) was used as a monitoring light. A Si−PIN photodiode (Hamamatsu Photonics, S1722-02) attached to a monochromator (Ritsu, MC-10N) was employed as a detector for the spectra in the visible and near-IR regions (360−1000 nm). For the absorption spectra in the near-IR region (600−1600 nm), a Ge avalanche photodiode (APD, Hamamatsu Photonics, B2834) was used as a detector. The output signal from the detector was recorded with a digitizing oscilloscope (Hewlett-Packard, 55410B) and analyzed using a personal computer.[20] All the sample solutions for the laser flash photolysis were contained in a 1 cm quartz cell and were deaerated by an argon bubbling (15 min).

Steady-state absorption spectra were recorded on a JEOL V-570DS spectrophotometer. Optical path length for the absorption spectrum measurements was either of 1 cm or 5 mm.

Results and Discussion

Ground and Excited State Properties. An absorption spectrum of $C_{120}O$ in toluene showed a different feature from that of C_{60}, but is similar to those of 1,2-adducts of C_{60} ($C_{60}R$):[21] Absorption peaks appeared at 691, 535 (sh), 418 (sh), and 327 nm (Figure 2). Compared to $C_{60}R$, the absorption peak at 691 nm is blue-shifted by 17−23 nm (348−466 cm^{-1}). It is worth mentioning that the observed shift agrees well with the difference between the first two reduction potentials of $C_{120}O$ (39 mV) which corresponds to 315 cm^{-1}.[12]

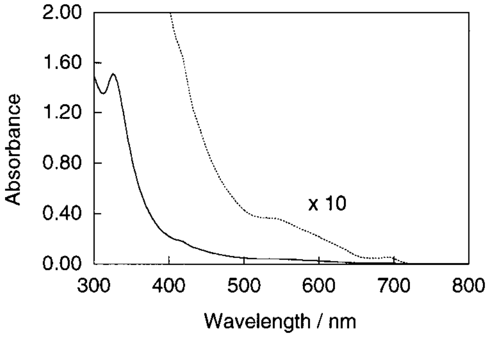

Figure 2. Steady-state absorption spectra of $C_{120}O$ (3.0×10^{-2} mM) in toluene. Optical path length was 1 cm.

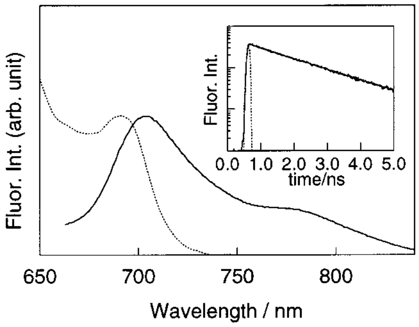

Figure 3. Steady-state fluorescence (solid line) and absorption (dot line) spectrum of $C_{120}O$ in toluene. Inset: Fluorescence intensity−time profile at 720 nm.

$C_{120}O$ in toluene showed a fluorescence peak at 705 nm accompanying a shoulder around 780 nm (Figure 3). Spectral features show almost a mirror image with the absorption spectrum in the region of 650−700 nm. The peak position is also blue-shifted compared to those of $C_{60}R$ (708−714 nm),[21] resulting from the blue shift of the corresponding absorption band. The singlet energies are listed in Table 1. The Stokes shift was estimated to be 288 cm^{-1}, which is larger than those of $C_{60}R$ (120−141 cm^{-1}).[21] This finding will suggest a structural relaxation in the singlet excited state of the present dimer molecule. The lifetime and fluorescence quantum yield (Φ_F) of $C_{120}O$ were estimated to be 1.7 ns (inset of Figure 3) and 8.7×10^{-4}, respectively, by adopting the Φ_F value of C_{60} in toluene as a reference (3.2×10^{-4}).[22] Higher Φ_F value than that of C_{60} can be attributed to a reduction of the structural symmetry of the C_{60} moiety. The fluorescence lifetime of $C_{120}O$ is similar to that of C_{120} (1.6 ns),[17] while it is longer than those of C_{60} (1.2 ns) and $C_{60}R$ (1.2−1.3 ns).[21]

With the laser-light excitation of $C_{120}O$ in toluene, transient absorption bands appeared at 630 and 480 nm with broad bands around 900 and 700 nm (Figure 4a). The absorption edge extended to ~1100 nm. These absorption bands can be attributed to the triplet excited state of $C_{120}O$ ($^3C_{120}O^*$), because these absorption bands were efficiently quenched in the presence of oxygen, a triplet energy acceptor: The quenching rate constant of $^3C_{120}O^*$ by oxygen (k_{ent}) was estimated to be 1.9×10^9 M^{-1} s^{-1}.

Furthermore, a generation profile of the main transient absorption band at 630 nm was observed by the picosecond laser photolysis as indicated in Figure 4b. The generation rate constant was estimated to be 4.2×10^8 s^{-1}, which is similar to the fluorescence decay rate constant. This agreement supports the generation of the transient absorption bands at 630 and 480 nm via the intersystem crossing process.

Compared with $^3C_{60}R^*$, the absorption band of $^3C_{120}O^*$ at 630 nm is blue-shifted (Table 1), accompanied by a broad

TABLE 1: Photophysical and Photochemical Properties of Some Fullerenes in the Excited States

	C_{60}	$C_{60}R^{a}$	$C_{120}{}^{b}$	$C_{120}O$
singlet properties[c]				
singlet energy (eV)	1.7	1.8	1.7	1.8
lifetime (ns)	1.2	1.2−1.3	1.6	1.7
Φ_F	3.2×10^{-4}	$(1.0-1.2) \times 10^{-3}$	7.9×10^{-4}	8.7×10^{-4}
triplet properties[c]				
T−T absorption (nm)	400, 740	680−700	<400, 700	480, 630
triplet energy (eV)	1.5	1.5	~1.5	1.2−1.3
lifetime (μs)	55	24−29	23	0.16
Φ_{isc}	1.0	0.88−0.95	0.70	0.48
photoinduced reaction rate constants via triplet state[d]				
ET with DABCO ($M^{-1}\,s^{-1}$)	3.2×10^9	2.0×10^{9e}	8.6×10^8	5.9×10^8
ET with TCNE ($M^{-1}\,s^{-1}$)	3.9×10^8	2.2×10^{9e}	1.2×10^9	no reaction

[a] From ref 21. [b] From ref 17 (in *o*-dichlorobenzene). [c] In toluene. [d] In benzonitrile. [e] Present study. Rate constant of the reaction of $C_{60}[(C_3H_6N)p\text{-}C_6H_4CHO]$.

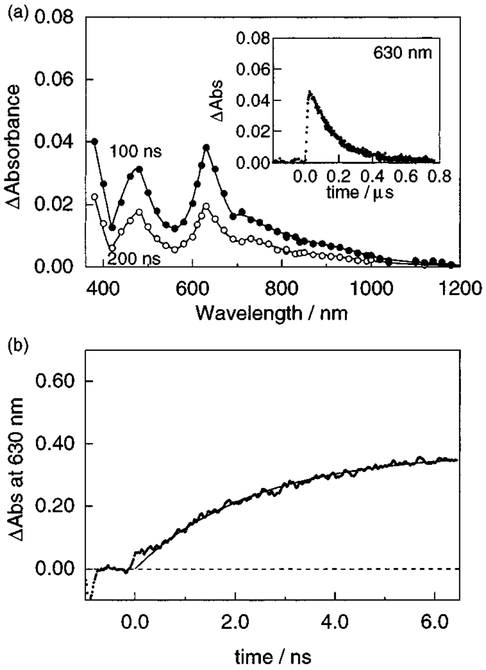

Figure 4. (a) Transient absorption spectra of $C_{120}O$ (3.0×10^{-2} mM) in toluene 100 and 200 ns after the laser irradiation (355 nm, fwhm 6 ns). Inset: Absorption−time profile at 630 nm. (b) Absorption−time profile at 630 nm by picosecond laser flash photolysis. Solid line is a fitted curve.

absorption band at the longer wavelength side (~1100 nm). From an absorption−time profile at 630 nm, the decay rate constant of ${}^3C_{120}O^*$ was estimated to be $6.3 \times 10^6\ s^{-1}$, which corresponds to 160 ns of the triplet-state lifetime (inset of Figure 4a). The lifetime did not depend on the excitation power within the examined range (1−14 mJ/pulse at 355 nm). This finding excludes deactivation of ${}^3C_{120}O^*$ by intermolecular and/or intramolecular triplet−triplet (T−T) annihilation under the present experimental conditions. The lifetime of ${}^3C_{120}O^*$ is quite shorter than those of C_{60} (55 μs), $C_{60}R$ (24−29 μs),[21] and C_{120} (23 μs).[17] Such quite short triplet lifetime of $C_{120}O$ will result from vibrations of the bonds connecting two C_{60} moieties which may efficiently quench the triplet state by means of the radiationless process. Recently, it has been reported by Weisman et al. that triplet-state lifetime of $C_{60}O$ including a C−O−C bond is 4.2 μs,[23] which is shorter than those of C_{60} etc. They proposed that the activated decay channel involves a reversible cleavage of the C−C epoxide bond. Therefore, a similar decay channel seems to be possible for ${}^3C_{120}O^*$. On the other hand, the T−T absorption peak of $C_{120}O$ is 630 nm, which is much different from those of $C_{60}O$ (710 nm) and other C_{60} derivatives. Therefore, such unusual triplet properties of $C_{120}O$ cannot be attributed to a C−O−C bond only. In the present case, participation of the CT states to the deactivation process of the triplet excited states, which are observed in the singlet excited 9,9′-bianthryl[24] and porphyrine dimers,[25] can be neglected, because the present solvent is nonpolar toluene and, furthermore, any absorption bands due to the radical ions were not observed in the transient absorption spectra.

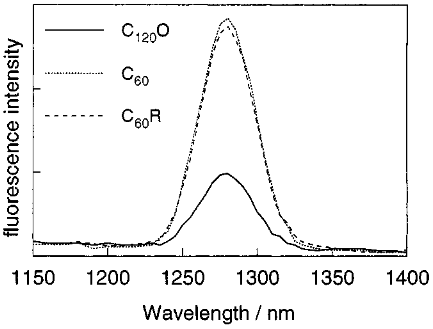

Figure 5. Luminescence spectra of ${}^1O_2$ generated by Ar ion laser excitation (488 nm) of $C_{120}O$ (solid line), C_{60} (dot line), and $C_{60}R$ ($C_{60}[(C_3H_6N)\text{-}p\text{-}C_6H_4CHO]$, broken line) in oxygen-saturated toluene. Absorbance of the samples were matched at the excitation wavelength.

After repeated laser irradiations of $C_{120}O$ (photon number for a laser shot was ca. 1×10^{19} photon cm^{-2} $pulse^{-1}$), no change was observed in a steady-state absorption spectrum. This finding indicates that $C_{120}O$ is quite stable to the laser irradiation as reported for other fullerenes, such as C_{60}, C_{70}, and C_{76}.[15b]

As mentioned in the above section, ${}^3C_{120}O^*$ was quenched by several triplet quenchers, such as oxygen and tetracene. Quenching by oxygen can be attributed to the triplet energy-transfer process (eq 1):

$$C_{120}O \xrightarrow{h\nu} {}^1C_{120}O^* \xrightarrow{isc} {}^3C_{120}O^* \xrightarrow[+O_2]{k_{ent}} C_{120}O + {}^1O_2^* \qquad (1)$$

Generation of ${}^1O_2^*$ was confirmed by the observation of the luminescence in the near-IR region. In Figure 5, the luminescence of ${}^1O_2^*$ generated via ${}^3C_{120}O^*$ was shown as well as those generated via the triplet excited C_{60} and $C_{60}R$ ($C_{60}[(C_3H_6N)\text{-}p\text{-}C_6H_4CHO]$). Luminescence intensity of ${}^1O_2^*$ via ${}^3C_{120}O^*$ is quite weak compared with those generated via ${}^3C_{60}^*$ and ${}^3C_{60}R^*$, even though the absorbance was matched at the excitation wavelength (488 nm). The generation yield of ${}^1O_2^*$ ($\Phi_{{}^1O_2}$) was estimated to be 0.35 ± 0.02 using $\Phi_{{}^1O_2}$ of ${}^3C_{60}^*$ as a standard ($\Phi_{{}^1O_2} = 0.96 \pm 0.04$).[26] The $\Phi_{{}^1O_2}$ value can be expressed as follows (eq 2):

$$\Phi_{^1O_2} = \{k_{ent}/(k_T + k_{ent}[O_2])\}\Phi_{isc} \quad (2)$$

where k_T and Φ_{isc} refer to the triplet decay rate constant of $^3C_{120}O^*$ without quencher and to the quantum yield for the intersystem crossing process, respectively. By employing the values estimated in the above sections and eq 2, the Φ_{isc} value was estimated to be 0.48. Furthermore, by using the relative actinometry using C_{60} as a standard (extinction efficient, $\epsilon = 16\,100\ M^{-1}\ cm^{-1}$ at 750 nm),[27] the ϵ value of $^3C_{120}O^*$ was estimated to be 7700 $M^{-1}\ cm^{-1}$ at 630 nm. The estimated Φ_{isc} value and the ϵ value are about a half of those of C_{60}, $C_{60}R$ and C_{120}.

Phosphorescence of $C_{120}O$ was not observed even in an iodoethane−toluene mixed solvent at 77 K, probably due to the considerably short lifetime of $^3C_{120}O^*$. The transient absorption bands due to $^3C_{120}O^*$ in toluene were quenched in the presence of tetracene (triplet energy = 1.27 eV)[28] at $9.4 \times 10^8\ M^{-1}\ s^{-1}$ of the reaction rate constant. On the other hand, $^3C_{120}O^*$ was not quenched by *trans*-retinol ($k_{ent} < 10^8\ M^{-1}\ s^{-1}$, triplet energy = 1.45 eV).[28] Therefore, it is concluded that the lowest triplet energy of $C_{120}O$ lies between 1.3 and 1.4 eV, which is lower value than those of C_{60}, $C_{60}R$, and C_{120}. These unusual properties of $^3C_{120}O^*$ indicate that the triplet excited C_{60} moiety in $^3C_{120}O^*$ was influenced by the adjacent π-electron system of another C_{60} moiety in the ground state.

Electron-Transfer Process in the Ground State. TDAE is an electron donor with a reduction potential $E(D/D^{\bullet+}) = -0.99$ V vs SCE.[29] It has been reported that TDAE and C_{60} form the radical ion salt which shows ferromagnetism at 16.1 K.[30] Recently, it became clear that fullerene (C_{60} or C_{70}) and TDAE are in equilibrium with the corresponding free-radical ions in polar solvents, while the radical ion pair formation is favorable in less polar solvents.[31] In the case of $C_{120}O$ in benzonitrile, which is a sufficiently polar solvent, a new absorption band appeared at 980 nm with shoulders at 810 and 600 nm on adding small amount of TDAE (Figure 6). Taking the oxidation potential of TDAE and the first reduction potential of $C_{120}O$ (−0.53 V)[12] into consideration, the new absorption bands in the visible and near-IR regions can be attributed to the radical anion of $C_{120}O$ ($C_{120}O^{\bullet-}$): The radical cation of TDAE is not reported to show any absorption band in the visible region.[32] The absorption bands of $C_{120}O^{\bullet-}$ increased with concentration of TDAE at constant concentration of $C_{120}O$. The finding indicates that the neutral molecules and the corresponding radical ions are in equilibrium as shown in eq 3:

$$C_{120}O + TDAE \rightleftharpoons C_{120}O^{\bullet-} + TDAE^{\bullet+} \quad (3)$$

The observation of $C_{120}O^{\bullet-}$ by the steady-state absorption spectra indicates that $C_{120}O^{\bullet-}$ is stable in contrast to $C_{120}^{\bullet-}$, which decomposed into C_{60} and $C_{60}^{\bullet-}$ immediately after the chemical reduction by TDAE.[17]

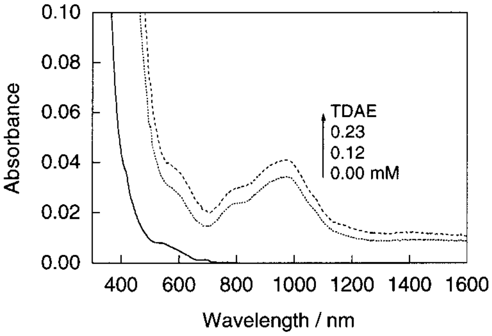

Figure 6. Steady-state absorption spectra of benzonitrile solution containing $C_{120}O$ (1.1×10^{-2} mM) and TDAE (optical path length 5 mm). Concentration of TDAE: 0, 0.12, and 0.23 mM.

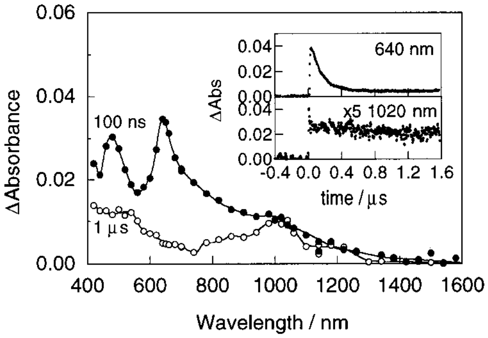

Figure 7. Transient absorption spectra of $C_{120}O$ (5.7×10^{-2} mM) in the presence of DABCO (2.7 mM) in benzonitrile irradiated by 355 nm laser. Inset: Absorption−time profiles at 640 and 1020 nm.

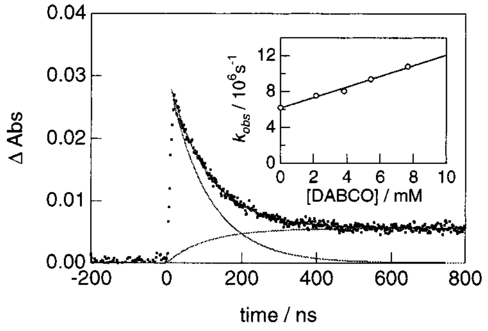

Figure 8. Absorption−time profile at 640 nm of the solution containing $C_{120}O$ and DABCO after 355 nm laser excitation. Fitted line was estimated by assuming decay of $^3C_{120}O^*$ and rise of $C_{120}O^{\bullet-}$. Inset: Relation between decay rate constant (k_{obs}) at 640 nm and concentration of DABCO.

Electron-Transfer Processes in the Excited State. $C_{120}O$ was selectively excited by the 355 nm laser irradiation of the benzonitrile solution containing $C_{120}O$ and DABCO, an electron donor. Immediately after the laser pulse, the absorption bands of $^3C_{120}O^*$ were confirmed, while new absorption bands appeared at 1000 and 550 nm in the spectrum at 1 μs after the excitation (Figure 7). The new absorption band at 1000 nm can be attributed to $C_{120}O^{\bullet-}$, since the observed absorption band shows good agreement with the one that appeared by the chemical reduction of $C_{120}O$ by TDAE (Figure 6). The absorption band at 550 nm is due to both $C_{120}O^{\bullet-}$ and the radical cation of DABCO ($DABCO^{\bullet+}$).[33] The decay of $^3C_{120}O^*$ (Inset of Figure 7) was accelerated with an increase in the concentration of DABCO. The finding indicates that $C_{120}O^{\bullet-}$ was generated by the electron-transfer process from DABCO to $^3C_{120}O^*$ (eq 4):

$$C_{120}O \xrightarrow{h\nu(355\ nm)} {}^1C_{120}O^* \xrightarrow{isc} {}^3C_{120}O^* \xrightarrow[+DABCO]{k_q^T} C_{120}O^{\bullet-} + DABCO^{\bullet+} \quad (4)$$

From the relation between the concentration of DABCO and the decay rate of $^3C_{120}O^*$ (k_{obs}), which was estimated by assuming the absorption−time profile at 640 nm is composed of the decay and rise of $^3C_{120}O^*$ and $C_{120}O^{\bullet-}$, respectively (Figure 8), the bimolecular quenching rate constant of $^3C_{120}O^*$ (k_q^T) was estimated to be $5.9 \times 10^8\ M^{-1}\ s^{-1}$ (inset of Figure 8). It is interesting to note that this k_q^T value is one order smaller than the diffusion-limiting rate constant of the solvent ($k_{diff} = 5.3 \times 10^9\ M^{-1}\ s^{-1}$ in benzonitrile at 25 °C),[28] in spite of the

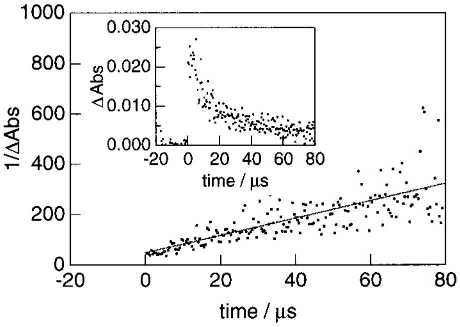

Figure 9. Second-order plot of absorption−time profile at 420 nm of the solution containing $C_{120}O^{\bullet-}$ and $DABCO^{\bullet+}$. Insert: Absorption−time profile at 420 nm.

sufficiently negative free energy change (−25 to −38 kJ mol^{-1}) for the electron-transfer process, which was estimated by using the Rehm−Weller equation.[34] In the case of the photoinduced electron-transfer process of C_{60} and DABCO in benzonitrile, the k_q^T value was estimated to be 3.2×10^9 M^{-1} s^{-1}.[35] As for $C_{60}[(C_3H_6N)p\text{-}C_6H_4CHO]$, one of the $C_{60}R$, the observed k_q^T value was 2.0×10^9 M^{-1} s^{-1}. The smaller k_q^T value with DABCO than the k_{diff} value was also observed in the electron-transfer process of the excited triplet state of C_{120}.[17] The deviations from the expected values (i.e., k_{diff}) will result from underestimation of encounter distance of the radical ion pair. In the above free energy calculation, the encounter distance was assumed to be 7 Å, which is often employed for the electron-transfer processes of small molecules.[34,36] Larger encounter distance of $C_{120}O$ or C_{120} makes the free-energy change for electron-transfer shifts to the positive direction, which leads to smaller k_q^T than the k_{diff} value.

The generated radical ions decayed over a 100 μs after reaching a maximum (inset of Figure 9). The decay of the radical ions can be attributed to the back electron transfer between the generated radical ions (eq 5), because any photochemical products were not confirmed in the steady-state absorption spectrum of the solution after hundred shots of the laser pulse irradiation.

$$C_{120}O^{\bullet-} + DABCO^{\bullet+} \xrightarrow{k_{bet}} C_{120}O + DABCO \qquad (5)$$

Actually, the second-order plot of the absorption−time profile shows a good linearity as shown in Figure 9. The k_{bet}/ϵ value was estimated to be 3.4×10^6 cm s^{-1} at 420 nm. The ϵ value is the sum of those of $C_{120}O^{\bullet-}$ and $DABCO^{\bullet+}$ and will be the order of 10^3 M^{-1} cm^{-1} at 420 nm. Therefore, the k_{bet} value is expected to be $>10^9$ M^{-1} s^{-1}, indicating that the generated radical ions returned to their neutral forms at the rate constant close to the k_{diff} value.

Photoinduced reduction of $C_{120}O$ was also confirmed with other electron donors. When tetrabutylammonium tetraphenylborate was used as an electron donor, accumulation of $C_{120}O^{\bullet-}$ in the solution was observed by a generation of the absorption band at 980 nm upon steady-state illumination of the visible light (>400 nm). The accumulation of $C_{120}O^{\bullet-}$ can be attributed to decomposition of tetraphenylborate anion radical after the electron transfer.[37] Because of the absence of the back electron transfer, persistent generation of $C_{120}O^{\bullet-}$ was confirmed as in the case of the ground-state reduction by TDAE.

Photoinduced Oxidation of $C_{120}O$. In recent papers, we have reported photochemical generation of the radical cation of fullerenes (C_{60}, C_{70}, C_{76}, C_{82}, and C_{120}) by employing the adequate electron acceptor and/or cosensitizer.[17,38,39] In the present paper, we attempted one-electron oxidation of $C_{120}O$. When $C_{120}O$ was excited in the presence of TCNE, any transient species due to oxidation product were not observed. Furthermore, acceleration of the decay of $^3C_{120}O^*$ was not confirmed ($<10^8$ M^{-1} s^{-1}). In the case of C_{120}, the laser irradiation in the presence of TCNE generated the radical cation of C_{120}. Poor reactivity of $^3C_{120}O^*$ with TCNE can be explained on the basis of the free-energy change for the photoinduced process. From the Rehm−Weller equation, the free-energy change was expected to be −3 to −12 kJ mol^{-1};[40] such smaller free-energy change resulted from smaller triplet energy of $C_{120}O$. It can be concluded that the small free-energy change and the short lifetime of $^3C_{120}O^*$ made observation of the oxidation process difficult.

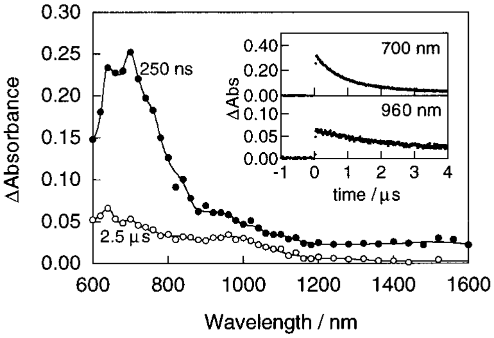

Figure 10. Transient absorption spectra observed by 355 nm laser excitation of NMA (0.2 mM) in the presence of $C_{120}O$ and BP (200 mM) in benzonitrile. Inset: Absorption−time profiles.

Oxidation of $C_{120}O$ was also attempted by a cosensitization method, which was demonstrated by Nonell et al. for the oxidation of C_{60}.[41] Figure 10 shows transient absorption spectra of the benzonitrile solution containing NMA, BP, and $C_{120}O$. Upon 355 nm laser excitation of the solution, a transient absorption band appeared around 700 nm, which was attributed to the radical cation of BP generated by eq 6:

$$NMA^+ \xrightarrow{h\nu} {}^1NMA^+ \xrightarrow{+BP} NMA^\bullet + BP^{\bullet+} \qquad (6)$$

At 2.5 μs after the laser irradiation, a new absorption band was confirmed at 960 nm, which can be attributed to the radical cation of $C_{120}O$ generated by eq 7:

$$BP^{\bullet+} + C_{120}O \rightarrow BP + C_{120}O^{\bullet+} \qquad (7)$$

The peak position of the radical cation of $C_{120}O$ is similar to that of $C_{60}^{\bullet+}$.[40] From the change of decay rates of $BP^{\bullet+}$ in the presence and absence of $C_{120}O$, the reaction rate constant for eq 7 was estimated to be 1×10^{10} s^{-1}, indicating an effective radical cation generation as observed in other fullerenes.[38,39,41]

The photophysical and photochemical parameters estimated in the present work are summarized in Table 1 as well as those of C_{60}, $C_{60}R$, and C_{120}. In Table 1, the properties of $^3C_{120}O^*$ are much different from those of $^3C_{120}^*$, indicating the specific interaction of C_{60}-moieties.

Conclusion

In the present paper, we examined the photophysical and photochemical properties of a fullerene dimer, $C_{120}O$. Properties of $^3C_{120}O^*$ are quite different from those of C_{60}, $C_{60}R$, and C_{120}. These unusual properties of $^3C_{120}O^*$ indicate that the triplet excited C_{60} moiety in $^3C_{120}O^*$ was influenced by the adjacent π-electron system of another C_{60} moiety in the ground state. Therefore, the distance between two fullerene moieties seems to be important for the properties of the excited triplet state. The photoinduced reduction and oxidation processes of $C_{120}O$ were also observed by the transient absorption measurements. The reaction rate constant of reduction process was slower than the diffusion-controlled limit of the solvent, in spite of the negative free energy changes calculated for these processes, in contrast to C_{60} and $C_{60}R$. This tendency will result from the larger size of fullerene dimer ($C_{120}O$ or C_{120}), which makes electron transfer unfavorable because of less stabilization of the radical ions due to smaller columbic energy.

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