

Photophysical and Photochemical Processes of an Unsymmetrical Fullerene Dimer, C₁₂₁Mamoru Fujitsuka,[†] Osamu Ito,^{*,†} Nita Dragoe,^{*,‡} Seitaro Ito,[‡] Hidekazu Shimotani,[‡] Hidenori Takagi,[‡] and Koichi Kitazawa[‡]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Katahira 2-1-1, Sendai 980-8577, Japan, and Department of Applied Chemistry, University of Tokyo, Tokyo 113-8656, Japan**Received: February 3, 2002; In Final Form: June 19, 2002*

Photophysical and photochemical processes of C₁₂₁, an unsymmetrical fullerene dimer, have been investigated by using laser flash photolysis mainly. The triplet excited state of C₁₂₁ showed a transient absorption band at 750 nm, whose deactivation process was governed by mixed-order kinetics of first and second order, indicating the contribution of triplet–triplet annihilation process. The intrinsic lifetime of the triplet excited state was estimated to be 13 μ s. The singlet and triplet excited states of C₁₂₁ are considered to be localized on one fullerene moiety of the two-fullerene cages. The one- and two-electron reductions of C₁₂₁ were observed in the presence of tetrakis(dimethylamino)ethylene in the ground state. The dianion of C₁₂₁ showed an absorption band in shorter-wavelength side due to the interaction of the transition dipole of anion radical on each fullerene cage of C₁₂₁. Photoinduced one-electron reduction of C₁₂₁ was confirmed in the presence of *N,N,N',N'*-tetramethyl-1,4-phenylenediamine as a donor. The reaction rate constant was close to the diffusion limiting rate because of the sufficiently negative free energy change of the reduction process via the triplet excited C₁₂₁. On the other hand, one-electron oxidation of the triplet excited state of C₁₂₁ was confirmed in the presence of tetracyanoethylene as an electron acceptor in a moderately polar solvent such as *o*-dichlorobenzene.

Introduction

Fullerenes have been widely investigated in the past decade because of their interesting properties, which are applicable to optical and electronic devices.¹ Various synthetic efforts have been performed in order to induce favorable properties to the fullerenes: For example, photovoltaic effect can be achieved by connecting an electron donor to a fullerene.^{2–7} Nowadays, several kinds of bond formations have been reported between fullerenes and other molecules.¹ It should be noted that the properties of fullerene derivatives depend on the structures of chemical bonds connecting a fullerene and other molecules. For example, fullerene derivatives with [6.6] closed structure, methanofullerenes, show different absorption spectra from fullerene derivatives with [5.6] open structure, homofullerenes (lower panel of Figure 1).⁸

Fullerenes also react with fullerene themselves to generate fullerene dimers, oligomers, and polymers.⁹ It has been reported that fullerene polymers are generated under several conditions.^{9–12} As for fullerene dimers, C₁₂₀, C₁₂₀O, C₁₂₁, C₁₂₂, C₁₁₈N₂, etc. have already been reported.^{13–16} Among them, C₁₂₀, C₁₂₁, and C₁₂₂ are all-carbon fullerene dimers. In the case of C₁₂₀, two fullerene cages are connected by a [2+2] type bond formation. As for C₁₂₁ and C₁₂₂, several isomers are possible. From theoretical and spectral studies, Dragoe et al. reported that the major isomer of C₁₂₁ has a spiro carbon atom bridge that connects to one of the fullerene cages through an open [5.6] junction and to the other through a closed [6.6] ring junction (Figure 1).¹⁵ That is, the major isomer of C₁₂₁ has an unsymmetrical structure composed of homofullerene and methanofullerene.

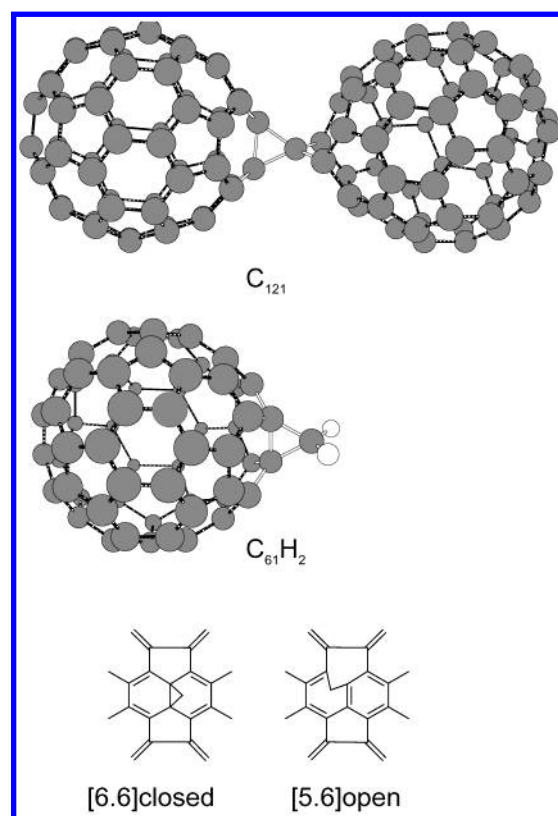


Figure 1. Molecular structures of C₁₂₁ and C₆₁H₂. Lower part: [6.6] closed (methanofullerene) and [5.6] open (homofullerene) structures of fullerene derivatives.

Photophysical and photochemical properties of fullerene dimers and trimers have been investigated by several groups.^{17–20} In the cases of C₁₂₀, C₁₂₀O, C₁₈₀, and C₁₁₈N₂, their singlet and

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triplet properties have been characterized by various methods, such as the laser flash photolysis.^{17–20} Their properties have been discussed in connection with those of fullerene polymers. Furthermore, aza–fullerene dimer, C₁₁₈N₂, has been applied to a photosensitizer of oxidation of olefins.²⁰ C₁₂₁ is expected to show interesting properties in the ground and excited states, because of its unsymmetrical structure.

In the present paper, we studied photophysical and photochemical properties of C₁₂₁ using laser flash photolysis method mainly. The properties of C₁₂₁ are compared with those of other fullerene dimers (C₁₂₀), methanofullerene (C₆₁H₂, Figure 1), and pristine C₆₀. Interactions between fullerene cages in the various states will be discussed.

Experimental Section

Materials. C₁₂₁ was synthesized as described in the previous report.¹⁵ The purity of the sample was >90%. *N,N,N',N'*-tetramethyl-1,4-phenylenediamine (TMPD) was prepared from its dihydrochloride (Kanto Chemicals) by neutralization with NaOH just before use. Tetracyanoethylene (TCNE) was purchased from Nacalai Tesque and purified by recrystallization from CH₂Cl₂. 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 limited solubility of C₁₂₁ in other solvents. To avoid degradation, we prepared all sample solutions just before the measurements.

Apparatus. Nanosecond transient absorption spectra in the near-IR region (600–1600 nm) were measured using second-harmonic generation (SHG, 532 nm) of a Nd:YAG laser (Spectra-Physics, Quanta-Ray GCR-130, fwhm 6 ns) as an excitation source. Monitoring light from a pulsed Xe-lamp was detected with a Ge-APD (Hamamatsu Photonics, B2834). For spectra in the visible region (400–1000 nm), a Si–PIN photodiode (Hamamatsu Photonics, S1722–02) was used as the detector. Triplet lifetime was estimated using a photomultiplier tube. Details of the transient absorption measurements were described in our previous reports.^{2c,6b,c,e,7g,17b,18,19,20b} All the samples were measured in a quartz cell (1 × 1 cm) and were deaerated by bubbling argon gas through the solution for 15 min.

Steady-state fluorescence spectra of the samples were measured on a Shimadzu RF-5300PC spectrofluorophotometer. Fluorescence spectra in the near-IR region were measured using an argon-ion laser (Spectra-Physics, BeamLok 2060-10-SA, 514 nm ca. 200 mW) as the 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 the 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 a 400 nm laser light.

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

Theoretical Calculations. All calculations were made using the Gaussian 98W package.²¹ Geometry optimization and estimations of molecular orbital coefficients were performed using the Becke-style 3 parameter density functional theory,

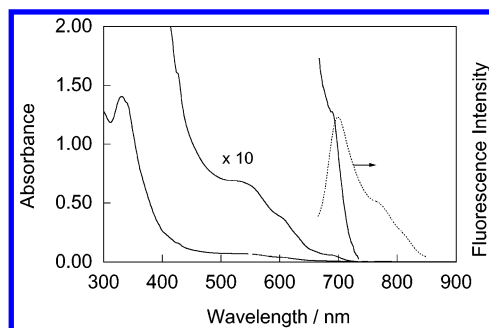


Figure 2. Absorption (solid line) and fluorescence (dot line) spectra of C₁₂₁ in DCB. Excitation: 410 nm.

using the Lee-Yang and Parr correlation functional, with 6-31 G(d) basis set.²²

Results and Discussion

Ground and Singlet Excited States of C₁₂₁. C₁₂₁ in DCB shows absorption bands at 689, 425, and 331 nm with shoulder bands around 600 and 530 nm (Figure 2). Dragoe et al. pointed out that the absorption spectrum of C₁₂₁ is similar to that of a mixture of a homofullerene and a methanofullerene.¹⁵ The 689 and 425 nm bands are characteristic of methanofullerene, while 600 and 530 nm bands are characteristic of homofullerene.^{8a} This finding indicates that C₁₂₁ has an unsymmetrical bis-fullerene structure.

From the molecular orbital calculation, the electron densities of HOMO and HOMO-1 are localized on methanofullerene moiety of C₁₂₁ (Figure 3). On the other hand, major part of the LUMO is located on homofullerene moiety, while minor part on methanofullerene moiety. The electron density of the LUMO+1 is localized on homofullerene moiety. Thus, the lowest electronic transition is expected to generate a CT-type excited state, which will show an absorption band in the longer-wavelength region. Since the ground-state absorption spectrum of C₁₂₁ does not show a band in the longer-wavelength side and is explained well by the superposition of those of homo- and methanofullerenes, contribution of the CT state seems to be small or negligible.

Upon excitation, C₁₂₁ showed fluorescence band at 699 nm with a shoulder around 750 nm (Figure 2). The Stokes shift was estimated to be 208 cm⁻¹, which is larger than those of methanofullerenes (120–141 cm⁻¹)^{2c} while smaller than that of C₁₂₀O (288 cm⁻¹).¹⁸ Thus, structural relaxation of C₁₂₁ in the singlet excited state will be smaller than that of C₁₂₀O. The fluorescence quantum yield of C₁₂₁ (Φ_F) was estimated to be 8.4 × 10⁻⁴ using pristine C₆₀ as a standard.²³ The estimated value is similar to those of C₁₂₀ (Φ_F = 7.9 × 10⁻⁴)^{17a} and C₆₁H₂ (Φ_F = 8.7 × 10⁻⁴) (Table 1). A 2- or 3-fold increase of the fluorescence quantum yield compared with that of pristine C₆₀ is a common feature of fullerene derivatives, of which structural symmetries are lower than C₆₀. The fluorescence lifetime of C₁₂₁ was estimated to be 1.3 ns from the single photon counting measurement. The estimated lifetime is shorter than those of C₁₂₀ (1.6 ns)^{17a} and C₁₂₀O (1.7 ns)¹⁸ but the same as those of pristine C₆₀ (1.3 ns) and C₆₁H₂ (1.3 ns) (Table 1).^{2c}

Triplet Excited State of C₁₂₁. In the laser flash photolysis experiment using the 532 nm laser light, C₁₂₁ showed a transient absorption band at 750 nm with a shoulder around 1000 nm (Figure 4). These transient absorption bands can be attributed to the triplet excited state of C₁₂₁, since the decay of the absorption band was accelerated in the presence of oxygen: The quenching of the triplet absorption band can be attributed to

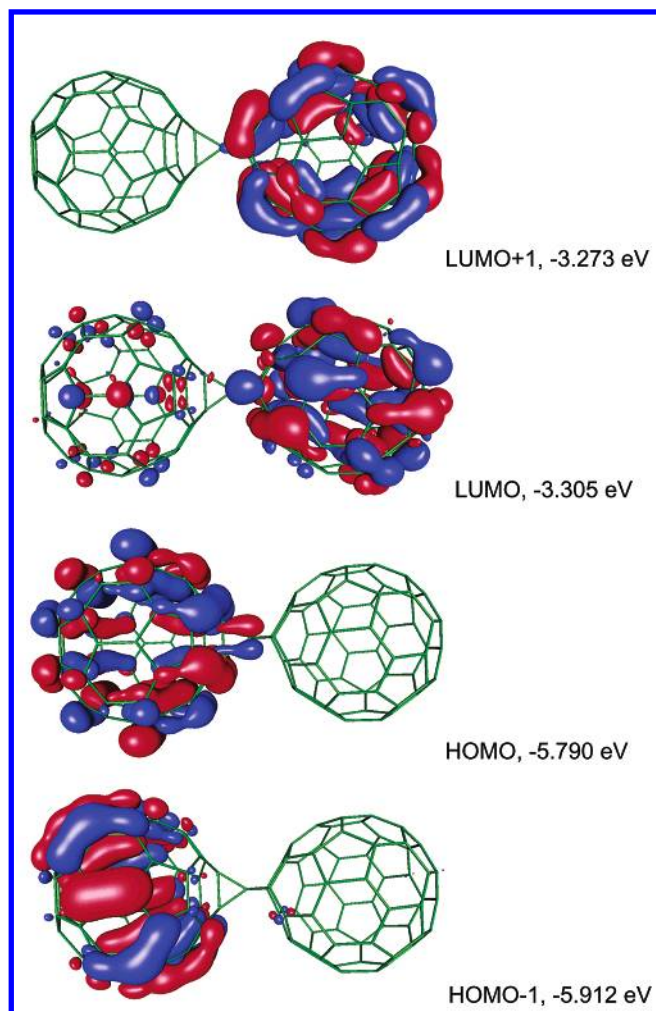


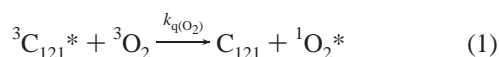
Figure 3. HOMO-1, HOMO, LUMO, and LUMO+1 of C₁₂₁.

TABLE 1: Photophysical and Photochemical Properties of C₁₂₁, C₁₂₀, C₆₁H₂, and C₆₀

	C ₁₂₁ ^a	C ₁₂₀ ^a	C ₆₁ H ₂	C ₆₀
Singlet ^b				
λ _F /nm	699	720	705 ^c	697 ^c
τ _F /ns	1.3	1.6	1.3 ^c	1.3 ^c
Φ _F	8.4 × 10 ⁻⁴	7.9 × 10 ⁻⁴	8.9 × 10 ^{-4 c}	3.2 × 10 ^{-4 c}
Triplet ^b				
λ _T /nm	750	700	710 ^c	750 ^c
τ _T ⁰ /μs	13	42 ^{c,d}	25 ^c	142 ^{c,d}
Φ _{ISC}	0.80	0.7	0.83 ^a	0.96 ^c
Reaction Rate Constant (k _q)/M ⁻¹ s ⁻¹				
k _q (TPMD)	2.6 × 10 ⁹ (1.5 × 10 ⁹) ^e	5.3 × 10 ⁹	2.6 × 10 ^{9 a}	5.9 × 10 ^{9 f}
k _q (TCNE)	9.7 × 10 ⁸	1.2 × 10 ⁹	1.2 × 10 ^{9 a}	3.9 × 10 ^{8 f}

^a In DCB. ^b λ_F, τ_F, Φ_F, λ_T, and τ_T⁰ referred to fluorescence peak position, fluorescence lifetime, fluorescence quantum yield, triplet peak position, and intrinsic lifetime of triplet, respectively. ^c In toluene. ^d From ref 17d. ^e k_{ET} value estimated from the relation k_{ET} = k_q × Φ_{ET}. ^f In benzonitrile.

the energy transfer process yielding the singlet oxygen (eq 1):



The bimolecular quenching rate constant of the energy transfer process (k_{q(O₂)}) was estimated to be 1.5 × 10⁹ M⁻¹ s⁻¹, indicating effective energy transfer process. The generation of

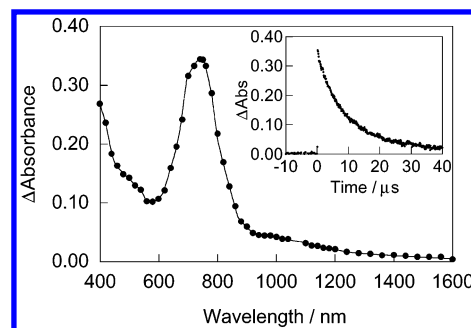


Figure 4. Transient absorption spectrum of C₁₂₁ (0.1 mM) in DCB at 100 ns after the 532 nm laser irradiation. Inset: Absorption–time profile at 750 nm.

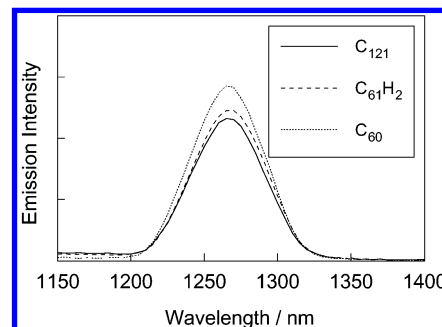


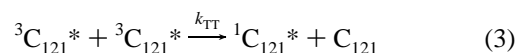
Figure 5. Emission spectra of singlet oxygen generated via ³C₁₂₁*, ³C₆₁H₂*, and ³C₆₀* in O₂-saturated DCB. Excitation: 514 nm.

the singlet oxygen can be confirmed by observation of an emission band of the singlet oxygen at 1265 nm (Figure 5). Emission spectra of singlet oxygen produced from the triplet states of C₆₀ and C₆₁H₂ are also shown in Figure 5, which were measured after the absorption intensities of the samples were matched with C₁₂₁ at the excitation wavelength (514 nm). The emission intensity of the singlet oxygen via ³C₁₂₁* is somewhat smaller than that via ³C₆₀*, indicating that the quantum yield for the triplet generation (i.e., the quantum yield for the intersystem crossing, Φ_{ISC}) of C₁₂₁ is smaller than that for C₆₀. The quantum yield for the singlet oxygen generation (Φ_{1O₂}) can be expressed using the Φ_{ISC} value as eq 2:

$$\Phi_{1\text{O}_2} = \Phi_{\text{ISC}} \times (k_{q(\text{O}_2)}[\text{O}_2]/(k_T + k_{q(\text{O}_2)}[\text{O}_2])) \quad (2)$$

where k_T is the decay rate of the triplet absorption band in the absence of oxygen. The Φ_{1O₂} value of C₁₂₁ was estimated to be 0.82 by using C₆₀ as a standard.²⁴ Thus, the Φ_{ISC} value of C₁₂₁ was estimated to be 0.80. Furthermore, from the relative actinometry method using C₆₀ as a standard,^{17d} an extinction coefficient (ε_T) of the absorption band of ³C₁₂₁* at 750 nm was estimated to be 1.0 × 10⁴ M⁻¹ cm⁻¹.

The triplet absorption band of C₁₂₁ decayed according to mixed-order kinetics of first- and second-order decay functions, indicating the contribution of the bimolecular process to the monomolecular process. Figure 6 shows that the absorption–time profiles of C₁₂₁ at 750 nm vary with excitation laser power. The absorption–time profiles deviate from first-order kinetics when the excitation laser power increases. This finding indicates that the triplet–triplet annihilation process (eq 3) contributes to the deactivation process of the triplet excited state:



From the laser power dependence of the triplet decay rate, the rate constant of the triplet–triplet annihilation process (k_{TT}) can

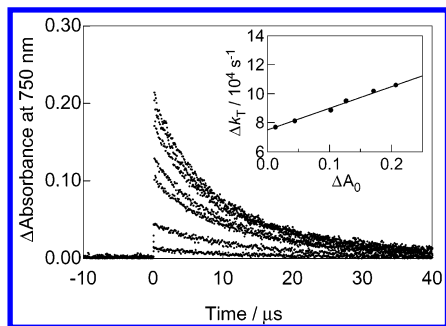


Figure 6. Absorption-time profiles of C₁₂₁ (0.1 mM) at 750 nm observed with various laser power. Inset: Relation between Δk_T and ΔA_0 .

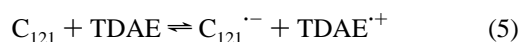
be estimated using relation expressed as eq 4:

$$-d[\ln(\Delta A_0)]/dt = \Delta k_T = k_T^0 + (2k_{TT}/\epsilon_T)\Delta A_0 \quad (4)$$

where ΔA_0 and k_T^0 are T–T absorbance at $t = 0$ and an intrinsic decay rate of the triplet excited state of C₁₂₁, respectively. As shown in an inset of Figure 6, the plot of Δk_T to ΔA_0 shows a linear relation. From the slope and the estimated ϵ_T value, the k_{TT} value was evaluated to be $7.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, which is one order of magnitude smaller value than the diffusion-limiting rate of the solvent ($k_{\text{diff}} = 5.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for DCB).²⁵ A k_{TT} value smaller by one order of magnitude than the k_{diff} value was also reported for other fullerenes, such as C₆₀ in benzene.²⁶ Thus, the triplet–triplet annihilation is not an effective deactivation process of the triplet states of the fullerenes. On the other hand, the k_T^0 value was estimated to be $7.5 \times 10^4 \text{ s}^{-1}$, which corresponds to 13 μs of the intrinsic lifetime (τ_T^0). The estimated τ_T^0 value is shorter than those of C₁₂₀ and C₆₁H₂ (Table 1). One of the reasons for the shorter lifetime will be a contribution of the self-quenching process. Thus, the present τ_T^0 value is the lowest limit of the triplet lifetime.

As shown in Table 1, the singlet and triplet excited-state properties of C₁₂₁ are similar to those of C₆₁H₂ and other fullerene derivatives. Thus, interaction between two fullerene cages of C₁₂₁ seems to be small in the singlet and triplet excited states, indicating localization of the excited states. The absorption peak position of ³C₁₂₁* is similar to that of ³C₆₀*,²⁷ i.e., a 60 π -electron system. On the other hand, triplet excited states of fullerenes with a 58 π -electron system such as methanofullerenes, pyrrolidinofullerenes, and dihydrofullerenes show triplet absorption band around 700 nm.^{1,8b,28} Thus, the triplet excited state of C₁₂₁ seems to be localized at homofullerene moiety of C₁₂₁.

Reduction of C₁₂₁ in the Ground State. It has been reported that the reduction process of C₁₂₁ proceeds sequentially on each of the two fullerene cages.¹⁵ The first two reduction potentials are –1.044 and –1.124 V vs ferrocene/ferricinium, which are similar to the first reduction potentials of pristine C₆₀.¹⁵ Thus, the chemical one-electron reduction processes of C₁₂₁ in the ground state are expected in the presence of a strong donor, such as tetrakis(dimethylamino)ethylene (TDAE).²⁹ Figure 7 shows absorption spectra of C₁₂₁ at various TDAE concentrations. By addition of small portion of TDAE, C₁₂₁ showed a new absorption band around 1160 nm, which can be attributed to the radical anion of C₁₂₁ generated by the process eq 5:



The first reduction potentials of the isomeric homofullerene and

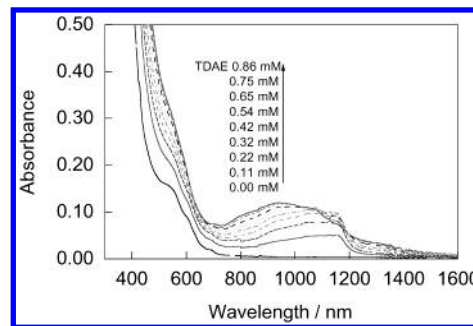
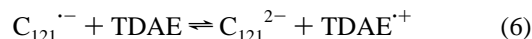


Figure 7. Absorption spectra of C₁₂₁ in the presence of TDAE at various concentrations in DCB.

methanofullerene are reported to be essentially identical.^{8a,30} The electrochemical reduction of homofullerene occurred at only 0.01 V anodic potential, as opposed to that of methanofullerene.^{8a,30b} Thus, the first reduction of C₁₂₁ possibly occurred on the homofullerene moiety. This consideration accords with the fact that the peak position of C₁₂₁^{•–} appeared at position close to C₆₀^{•–} (1080 nm),²⁹ compared to the peak position of methanofullerene (1040 nm).³¹ Furthermore, theoretical calculation indicates that the LUMO-level molecular orbital of C₁₂₁ is located mainly on homofullerene side of C₁₂₁ (Figure 3).

When further amounts of TDAE were added, an absorption band appeared at 945 nm with an isosbestic point around 1030 nm (Figure 7). The new absorption band at 945 nm can be attributed to dianion of C₁₂₁ by reduction process eq 6:



For the electronic structure of C₁₂₁^{2–}, two possibilities can be pointed out: dianion on one of the fullerene cages and bis-(radical anion). In the present case, bis(radical anion) seems to be adequate for C₁₂₁^{2–}, since the reduction of radical anion requires additional energy due to repulsion of electrons. Furthermore, the difference in the reduction potentials between isomeric homofullerene and methanofullerenes is quite small, as indicated above. Bis(radical anion) structure accords with the fact that small part of the LUMO is located on the methanofullerene moiety (Figure 3).

The observed absorption spectrum of the dianion is not merely a spectral overlap of the two radical anions: The absorption band at 945 nm appeared with decrease of the 1160 nm band. Thus, the appearance of the absorption band in the shorter-wavelength region indicates that the interaction between the transition dipoles of two radical anions on each fullerene cages exists in the dianion of C₁₂₁. The interaction between transition dipole moments can be supported by the fact that the peak position of C₁₂₁^{2–} is shifted to the shorter-wavelength side compared to the radical anion of C₆₁H₂ (1040 nm).³¹

Reduction of C₁₂₁ in the Triplet Excited State. Acceptor abilities of fullerenes are increased in their excited states. From the reduction potential, C₁₂₁ is also considered to be a good electron acceptor in its excited state. Photoinduced electron-transfer process was examined using *N,N,N',N'*-tetramethyl-1,4-phenylenediamine (TMPD) as an electron donor, as shown in transient absorption spectra in Figure 8. In the ground state, interaction between C₁₂₁ and TMPD can be ignored, since the ground-state absorption spectrum of a mixture of C₁₂₁ and TMPD was the same as the superposition of the spectra of the components. Immediately after the laser pulse irradiation, a transient absorption spectrum showed a peak at 750 nm, indicating formation of ³C₁₂₁*. At 1 μs after the laser pulse

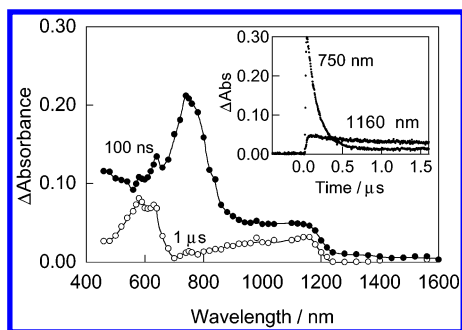
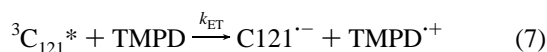


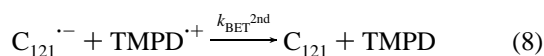
Figure 8. Transient absorption spectra of C_{121} (0.1 mM) in the presence of TMPD (2 mM) in DCB upon 532 nm laser irradiation. Inset: The absorption–time profiles at 1160 and 750 nm.

irradiation, the absorption band of ${}^3C_{121}^*$ decayed, and new absorption bands appeared at 1160, 640, and 580 nm. The absorption bands at 640 and 580 nm can be attributed to radical cation of TMPD.³² The absorption band at 1160 nm is the radical anion of C_{121} from the comparison with the spectra obtained by chemical reduction by TDAE (Figure 7). Appearance of the radical ions with the decrease of the triplet excited state of C_{121} indicates that the photoinduced electron-transfer proceeded from TMPD to the triplet excited state of C_{121} (eq 7):



From the relation between the decay rate of ${}^3C_{121}^*$ and concentration of TMPD, the bimolecular quenching rate constant of ${}^3C_{121}^*$ ($k_{\text{q(TMPD)}}$) was estimated to be $2.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, which is close value to the k_{diff} value of the solvent.²⁵ From the comparison of the absorption bands of $C_{121}^{\cdot-}$ with $\text{TMPD}^{\cdot+}$,³² an extinction coefficient of $C_{121}^{\cdot-}$ was estimated to be $2400 \text{ M}^{-1} \text{ cm}^{-1}$ at 1160 nm. Using the estimated extinction coefficients, we calculated the quantum yield for the present electron-transfer process ($\Phi_{\text{ET(TMPD)}}$) to be 0.58. This finding indicates that the other processes such as exciplex formation and/or collisional quenching exist in the deactivation pathway of the triplet excited C_{121} as well as electron transfer. In the present case, energy transfer can be ignored due to the lower triplet energy of C_{121} than TMPD. The electron-transfer rate constant ($k_{\text{ET(TMPD)}}$) was estimated to be $1.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ from the relation of $k_{\text{ET(TMPD)}} = k_{\text{q(TMPD)}} \times \Phi_{\text{ET(TMPD)}}$. Efficient electron-transfer process seems to be adequate, since the free energy change for the electron-transfer process via the triplet excited state of C_{121} was estimated to be $-97.6 \text{ kJ mol}^{-1}$, which is a sufficiently negative value for the fast electron transfer.

The absorption bands of the radical ions decayed over several tens of microseconds, as shown in the inset of Figure 9. Since any product formation was not confirmed in the ground-state absorption spectrum after the laser illuminations of the C_{121} -TMPD system, the decay of the radical ions can be attributed to the back electron transfer process between freely solvated radical ions (eq 8):



The decay profile of the radical ions was analyzed by the second-order plot as shown in Figure 9. The absorption band at 640 nm is due to the radical cation of TMPD as indicated above. The slope of the line in Figure 9 corresponds to $k_{\text{BET}}^{2\text{nd}}/(\text{extinction coefficient of } \text{TMPD}^{\cdot+})$, which was estimated to be $6.6 \times 10^6 \text{ cm s}^{-1}$ at 640 nm; thus, the $k_{\text{BET}}^{2\text{nd}}$ value was $4.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. The estimated value is larger than the diffusion

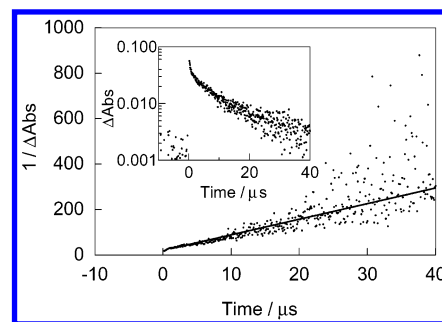


Figure 9. Second-order plot of the absorption–time profile of C_{121} (0.1 mM) in the presence of TMPD (2 mM) in DCB at 640 nm. Inset: First order plot of the absorption–time profile at 640 nm.

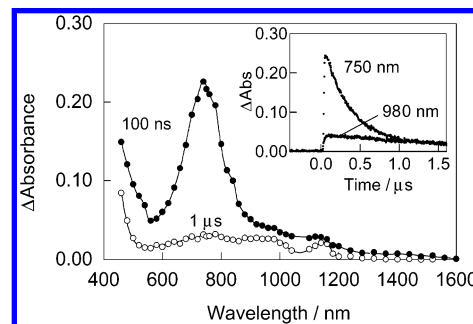
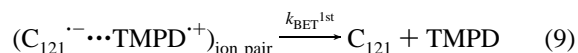


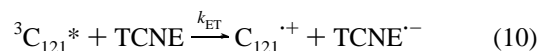
Figure 10. Transient absorption spectra of C_{121} (0.1 mM) in the presence of TCNE (2 mM) in DCB upon 532 nm laser irradiation. Inset: Absorption–time profiles at 980 and 750 nm.

limiting value of the solvent. Furthermore, slight deviation was observed in the latter part of the curve fitting. On the other hand, the decay profile cannot be fitted properly only by the first-order decay function as shown in the inset of Figure 9, indicating that the decay of the radical ions is governed by the mixed-order kinetics of first- and second-order decay functions. Mixing of first-order decay kinetics suggests that a part of the radical ions is present as radical ion pair, as shown in eq 9:



Formation of the radical ion pair in DCB was also confirmed for the electron-transfer processes of C_{60} with various aromatic amines.³³

Oxidation of C_{121} in the Triplet Excited State. As for oxidation process of fullerenes, there are limited number of papers.^{17b,34} Photoinduced oxidation of fullerenes can be achieved employing strong electron acceptors such as tetracyanoethylene (TCNE). Figure 10 shows transient absorption spectra of C_{121} in the presence of TCNE in DCB. Immediately after the laser pulse irradiation, the absorption band of ${}^3C_{121}^*$ appeared at 750 nm. At $1 \mu\text{s}$ after the laser excitation, new absorption bands appeared at 1140, 980, and $<400 \text{ nm}$ with the decay of ${}^3C_{121}^*$. The absorption bands at 1140 and 980 nm are attributed to the radical cation of C_{121} , while absorption band $<400 \text{ nm}$ is due to the radical anion of TCNE generated by the electron-transfer process (eq 10):



The electron-transfer mechanism (eq 10) is also supported by the fact that the decay of ${}^3C_{121}^*$ is accelerated by an increase of concentration of TCNE. From the relation between the decay rate of ${}^3C_{121}^*$ and concentration of TCNE, the bimolecular

quenching rate constant of TCNE with ³C₁₂₁* ($k_{q(\text{TCNE})}$) was estimated to be $9.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. The estimated $k_{q(\text{TCNE})}$ value is larger than that of pristine C₆₀ in benzonitrile ($k_{q(\text{TCNE})} = 3.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$), even though DCB is a less polar solvent than benzonitrile.²⁵ The finding indicates that the triplet excited C₁₂₁ has higher donor ability compared to pristine C₆₀.

Conclusion

From the photophysical and photochemical studies on C₁₂₁, it was revealed that C₁₂₁ generated the triplet excited state as effectively ($\Phi_{\text{ISC}} = 0.80$) as other fullerene derivatives upon photoexcitation. The singlet and triplet excited states of C₁₂₁ are considered to be localized on one fullerene moiety of the two-fullerene cages. The reactivity of the triplet excited C₁₂₁ was confirmed by observing transient absorption bands due to radical anion and cation of C₁₂₁. High electron acceptor ability of the triplet excited C₁₂₁ was confirmed. Furthermore, the electron donor ability of the triplet excited C₁₂₁ was higher than that of pristine C₆₀. Dianion of C₁₂₁ showed an absorption band in shorter-wavelength region due to the interaction of the transition dipole of anion radical on each fullerene cages of C₁₂₁.

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