

Laser Flash Photolysis Study on Photophysical and Photochemical Properties of C₈₂

Mamoru Fujitsuka, Akira Watanabe, and Osamu Ito*

Institute for Chemical Reaction Science, Tohoku University, Katahira, Aoba-ku, Sendai 980-8577, Japan

Kazunori Yamamoto and Hideyuki Funasaka

Nuclear Fuel Technology Development Division, Tokai Works, Power Reactor & Nuclear Fuel Development Corporation, Tokai, Ibaraki 319-1194, Japan

Takeshi Akasaka

Graduate School of Science and Technology, Niigata University, Niigata 950-2181, Japan

Received: June 16, 1999; In Final Form: August 25, 1999

Photophysical and photochemical properties of C₈₂ (C₂ isomer) have been examined by using a laser flash photolysis method. The transient absorption band of the triplet excited state was observed at 750 nm accompanying an absorption band tail in the near-IR region. The intrinsic triplet lifetime and intersystem crossing quantum yield were estimated to be 56 μ s and <0.01, respectively, which were smaller than those of C₆₀ and C₇₀. An absorption band of the radical anion of C₈₂ appeared at 897 nm by chemical reduction with donors such as tetrakis(dimethylamino)ethylene. Photoinduced reduction of C₈₂ was also observed by adopting *N,N,N',N'*-tetramethyl-1,4-phenylenediamine as a donor. By photosensitized reaction, oxidation of C₈₂ was confirmed. The reaction rate constant between C₈₂ and BP^{•+} was $1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, indicating effective radical ion formation as observed with other fullerenes (C₆₀, C₇₀, and C₇₆).

Introduction

Excitation–relaxation and photochemical processes of fullerenes have been extensively studied in recent years.^{1–6} Especially, charge transfer of fullerenes attracted much attention, because it results in not only synthetic reactions but also useful functions, such as photoconductivity,^{7,8} ferromagnetism,⁹ and superconductivity.¹⁰ In contrast to C₆₀ and C₇₀, studies on photophysics and photochemistry of higher fullerenes are quite rare, although their wide absorption ranging to the near-IR region is competent to light-active devices.

Excited-state properties of higher fullerenes, including C₇₆, C₇₈, and C₈₄, have been examined^{11–17} by laser flash photolysis, pulse radiolysis, and time-resolved EPR. The intersystem crossing quantum yields (Φ_{isc}) of higher fullerenes are 0.05 and 0.14 for C₇₆ and C₇₈, respectively,¹³ and almost zero for C₈₄.¹⁷ These values are rather low compared to the near unity value observed for C₆₀ and C₇₀.^{1c,2a}

As for C₈₂, nine isomers are expected from the isolated pentagon rule ($2 \times C_{3v}$, C_{2v} , $3 \times C_2$, and $3 \times C_s$).¹⁸ From ¹³C NMR study, Kikuchi et al. reported that one isomer of C₈₂ with C₂ symmetry is predominantly produced.^{19,20} Photophysics of C₈₂ have not been reported, although its photochemical addition reaction^{21,22} and electrochemical redox properties have been studied in connection to metal encapsulated fullerenes such as La@C₈₂, in which electron transfer occurs between the fullerene cage and metal.^{23,24} Studies on the excitation–relaxation process and photochemical behavior of C₈₂ seem to be important in fullerene chemistry, also with a view of elucidating structure-dependent properties of higher fullerenes.

In the present paper, we report the results of a laser flash photolysis study of C₈₂ (C₂ isomer). Its triplet properties and photoinduced reduction and oxidation reactions have been

examined by observing the transient absorption spectra in both the visible and near-IR regions.

Experimental Section

Materials. C₈₂ (C₂ isomer) was synthesized by evaporating a graphite rod using the contact arc method and purified by using an HPLC system. Both extraction and HPLC separation were done under anaerobic conditions. Details of the extraction and HPLC separation are described elsewhere.^{25,26} To remove fullerene oxides and C₈₂ minor isomers as well as other higher fullerenes from the C₈₂ major isomer, two types of HPLC columns were used at two temperatures (0 and 45 °C). Identification of C₈₂ was carried out using positive- and negative-ion Fourier transform ion cyclotron resonance mass spectrometers. Isomeric identification of C₈₂ (C₂) was confirmed by measuring ¹³C NMR spectroscopy (see Supporting Information).¹⁹ From the electrochemical (DPV and OSWV) and HPLC analyses, it was confirmed that minor isomers were completely removed from the C₈₂ sample of the present photophysical and photochemical studies. The purity of C₈₂ was >99%.

N-Methylacridinium hexafluorophosphate (NMA⁺) was synthesized by the procedure reported by Gebert et al.²⁷ *N,N,N',N'*-Tetramethyl-1,4-phenylenediamine (TMPD) was prepared from TMPD dihydrochloride (Kanto Chemicals) by neutralization with NaOH just before use. Other chemicals were of the best commercial grade available.

Apparatus. The nanosecond time-resolved absorption spectra were measured using SHG (532 nm) or THG (355 nm) of a Nd:YAG laser (Spectra-Physics, Quanta-Ray GCR-130, fwhm 6 ns) as the excitation source. A Ge-APD photodiode (Hamamatsu Photonics, B2834) was employed as the detector for spectra in the near-IR region (600–1600 nm). For spectra in the visible

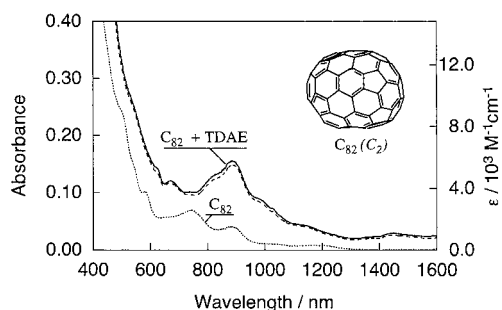


Figure 1. Absorption spectra of C_{82} (5.5×10^{-5} M) in the absence and presence of TDAE in benzonitrile (optical path: 5 mm). Concentration of TDAE; 0 (dot line), 7.1×10^{-5} (broken line), and 3.6×10^{-4} M (solid line). Inset: molecular structure of C_{82} (C_2 isomer).

region (500–1000 nm), a Si-PIN photodiode (Hamamatsu Photonics, S1722-02) was used as the detector. Triplet lifetime was estimated by using a Si-APD photodiode (Hamamatsu Photonics, S5343). Details of the laser flash photolysis method are described in a previous paper.¹¹ 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-570DS spectrophotometer. The optical path length for the absorption spectrum measurement was either 1 cm or 5 mm.

EPR spectra were measured with a Varian E-4. Typical microwave power was 5 mW. EPR measurements were carried out just after the sample preparation and deaeration.

Results and Discussion

Properties of C_{82} in the Ground State. C_{82} in toluene shows absorption bands at 1180, 880, 743, 583, and 364 nm accompanying a shoulder around 500 nm (Figure 1). The extinction coefficient (ϵ) was estimated as in Figure 1. Depending on size and symmetry, the absorption tail of higher fullerenes ranges to longer wavelength, which indicates a small HOMO–LUMO gap of higher fullerenes. Oxidation ($E(C_{82}^{+}/C_{82})$) and reduction ($E(C_{82}/C_{82}^{\bullet-})$) potentials of C_{82} in 1,2-dichlorobenzene are reported to be 0.72 and -0.69 V vs ferrocene/ferrocenium, respectively,²³ which correspond to 1.42 and 0.01 V vs SCE in benzonitrile.²⁸ Since these potentials are shifted to cathodic and anodic potentials, respectively, compared with those of C_{60} , C_{70} , and C_{76} ,²⁴ reduction of C_{82} in the ground state is expected to proceed more easily than reduction of C_{60} , C_{70} , and C_{76} .

Fluorescence and phosphorescence were not observed even at 77 K, as in the case of C_{76} ,¹¹ while C_{60} and C_{70} show weak fluorescence bands at 697 and 670 nm, respectively.²⁹

Electron Transfer of C_{82} in the Ground State. Tetrakis(dimethylamino)ethylene (TDAE) is one of the strongest organic donors. TDAE and C_{60} form a radical ion salt that shows ferromagnetism at low temperatures.⁹ Recently, it became clear that in polar solvents fullerene (C_{60} or C_{70}) and TDAE are in equilibrium with the corresponding free radical ions, while radical ion pair formation is favorable in less polar solvents.³⁰ In the case of C_{82} (5.5×10^{-5} M) in benzonitrile, new absorption bands appeared at 897 and 670 nm accompanying a shoulder around 1400 and 1000 nm by adding a small portion of TDAE (7.1×10^{-5} M) (Figure 1). The new absorption bands in the near-IR region can be attributed to the radical anion of C_{82} ($C_{82}^{\bullet-}$). TDAE⁺ does not show appreciable absorption in the visible region.

This identification is supported by the results of EPR measurements. In the EPR spectra of the C_{82} –TDAE mixture in benzonitrile/toluene (1:1) mixed solvent (Figure 2a), genera-

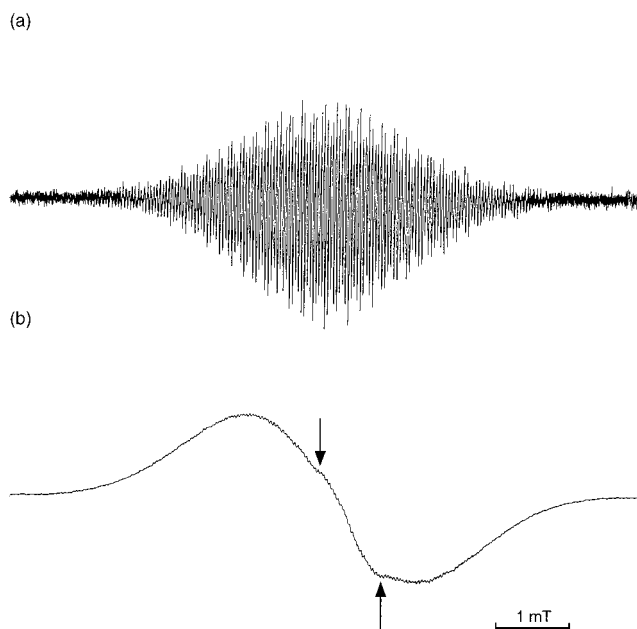
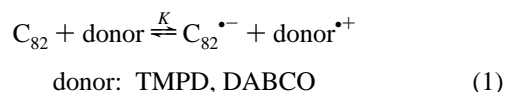


Figure 2. EPR spectra of a mixture of C_{82} (7×10^{-5} M) and TDAE (2×10^{-4} M) in deaerated benzonitrile/toluene (1:1) at room temperature. Modulation width: (a) 0.1 G and (b) 10 G.

tion of TDAE⁺ was confirmed: the observed hyperfine structure was analyzed well by assuming the reported coupling constants (4 N atoms with 0.49 mT, 12 H atoms with 0.33 mT, and 12 H atoms with 0.28 mT).³¹ By changing the modulation width, a weak signal that is superimposed on the signal due to TDAE⁺ is confirmed, as indicated by arrows (Figure 2b). The weak signal can be attributed to $C_{82}^{\bullet-}$. The g value is estimated to be 2.0021, which is in good agreement with reported values for higher fullerene–TDAE charge-transfer salts.³²

Since the absorbance of $C_{82}^{\bullet-}$ was not changed by adding an excess amount of TDAE, almost all C_{82} changed to the radical anion by adding a slight excess of TDAE. An extinction coefficient (ϵ) at 897 nm of $C_{82}^{\bullet-}$ was estimated to be 5.7×10^3 M^{−1} cm^{−1} by assuming that all C_{82} changed to $C_{82}^{\bullet-}$. The estimated ϵ value is of the same order as those of $C_{70}^{\bullet-}$ and $C_{76}^{\bullet-}$ (4.0×10^3 M^{−1} cm^{−1} at 1370 nm and 1.5×10^3 M^{−1} cm^{−1} at 880 nm, respectively)^{11,33} while smaller than that of $C_{60}^{\bullet-}$ (1.2×10^4 M^{−1} cm^{−1} at 1078 nm).³⁴

Reduction of C_{82} in the ground state was also confirmed in benzonitrile solution of C_{82} and TMPD or 1,4-diaza[2.2.2]-bicyclooctane (DABCO), which is not a strong electron donor in the ground state: The oxidation potentials ($E(D^{\bullet+}/D)$) are 0.16 and 0.57 V vs SCE, respectively. In the case of TMPD and C_{82} , absorption bands characteristic of the radical cation of TMPD (TMPD^{•+}) were confirmed at 618 and 569 nm³⁵ as well as the absorption band of $C_{82}^{\bullet-}$ in a difference absorption spectrum. Absorbance of $C_{82}^{\bullet-}$ increased with the concentration of donor, TMPD or DABCO. This finding indicates that C_{82} and TMPD or DABCO were in equilibrium with corresponding radical ions, as shown in eq 1, where K is an equilibrium



constant of the reaction. K values for the reactions with TMPD and DABCO were estimated to be 4.1×10^{-4} and 4.6×10^{-4} , respectively, by applying the procedure reported in our previous paper.³⁰ Therefore, in benzonitrile solution containing 5.5×10^{-5} M of C_{82} and 5.0×10^{-3} M of TMPD, which is a typical

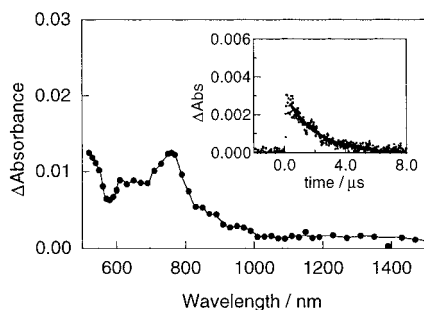


Figure 3. Transient absorption spectrum of C₈₂ (7×10^{-5} M) in toluene at 100 ns after laser irradiation (355 nm). Inset: absorption–time profile at 750 nm. The solid line is a fitted curve.

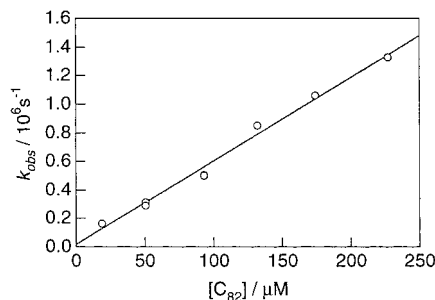
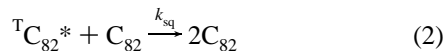


Figure 4. Relationship between the decay rate constant of C₈₂ (k_{obs}) at 750 nm and the concentration of C₈₂.

condition of the following laser flash experiments, 18% of C₈₂ is expected to be in the radical anion state: The absorption spectrum of the mixture can be well simulated by assuming the above components (see Supporting Information). It is worth mentioning that in the cases of C₆₀, C₇₀, and C₇₆, TMPD and DABCO do not generate corresponding radical ions in the ground states even in highly polar solvents, because the reduction potentials of C₆₀, C₇₀, and C₇₆ are sufficiently higher than the oxidation potentials of TMPD and DABCO. Therefore, largely extended π -conjugation of C₈₂ results in a lower reduction potential, which is favorable for radical ions formation.

Excited-State Properties of C₈₂. The transient absorption spectrum of C₈₂ in toluene shows absorption bands at 750 and <500 nm accompanying a shoulder around 600 nm and an absorption tail ranging to the near-IR region (Figure 3). The absorption band can be attributed to the triplet excited state of C₈₂, (³C₈₂*), since the absorption band was quenched in the presence of β -carotene, a triplet energy acceptor. When the solution contained 9.3×10^{-5} M C₈₂, the decay rate constant of the transient absorption band (k_{obs}) was estimated to be 5.1×10^5 s⁻¹, which corresponds to 2.0 μ s of lifetime (inset of Figure 3). The k_{obs} value was decreased when the concentration of C₈₂ in the solution decreased. The finding can be attributed to the self-quenching process (eq 2), where k_{sq} is a bimolecular



rate constant for the self-quenching process. The k_{obs} value and concentration of C₈₂ show a linear relationship as in Figure 4. From a slope and an intercept, the k_{sq} value and an intrinsic lifetime of ³C₈₂* were estimated to be 5.8×10^9 M⁻¹ s⁻¹ and 56 μ s, respectively. The intrinsic lifetime of ³C₈₂* is shorter than those of C₆₀ and C₇₀ (143 μ s and 11.8 ms in toluene at room temperature, respectively).³⁶ The short intrinsic lifetime seems to be characteristic of higher fullerenes, since an intrinsic lifetime of ³C₇₆* was reported to be 9.6 μ s.¹²

It is worth mentioning that the triplet absorption band of C₈₂ was not quenched by oxygen. Although it is well-known that

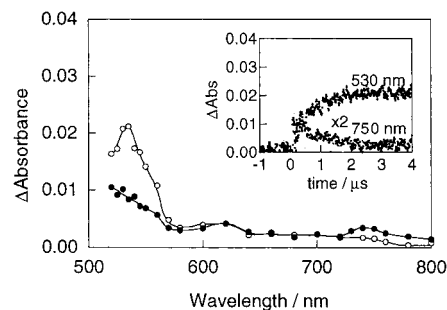
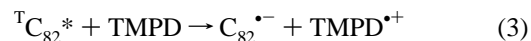


Figure 5. Transient absorption spectra of C₈₂ (7×10^{-5} M) and β -carotene (6.3×10^{-5} M) in benzonitrile at 250 ns (filled circles) and 2.5 μ s (open circles) after the 355 nm laser irradiation. Inset: absorption–time profiles at 750 and 530 nm.

triplet-excited fullerenes (C₆₀ and C₇₀) produce singlet oxygen at almost unity of quantum yield,³⁷ insensitivity to oxygen is reported for excited C₈₄.¹⁶ Thus, insensitivity of ³C₈₂* to oxygen is quite reasonable since the steady-state absorption band ranges to \sim 1300 nm; i.e., the triplet energy of C₈₂ should be lower than 94.1 kJ mol⁻¹, which is smaller than the energy for production of singlet oxygen (94.1 kJ mol⁻¹).³⁸ On the other hand, ³C₈₂* was quenched in the presence of β -carotene, as shown in Figure 5. The quenching of ³C₈₂* can be attributed to the triplet energy transfer to β -carotene, since the absorption band due to the triplet state of β -carotene was generated with a decrease of ³C₈₂* (inset of Figure 5). The bimolecular reaction rate constant was estimated to be 1.5×10^9 M⁻¹ cm⁻¹, which is smaller than the diffusion limiting rate of toluene (1.1×10^{10} M⁻¹ cm⁻¹). Therefore, the triplet energy of C₈₂ is considered to be lying between 88 and 94 kJ mol⁻¹.³⁸ Furthermore, from a comparison with the ϵ value of β -carotene (1.7×10^5 M⁻¹ cm⁻¹ in hexane),³⁹ ϵ of ³C₈₂* was estimated to be 2.4×10^4 M⁻¹ cm⁻¹ at 750 nm, which is on the same order with that of ³C₆₀* and ³C₇₆*.¹¹ Despite the appreciable ϵ value of ³C₈₂*, the transient absorption band of ³C₈₂* was quite small even by excitation with high laser power (30 mJ/pulse at 355 nm). This finding can be attributed to a very low quantum yield for intersystem crossing process (Φ_{isc}). Low Φ_{isc} values are also reported for other higher fullerenes, C₇₆ (0.05) and C₇₈ (0.12),¹³ while high Φ_{isc} values are reported to C₆₀ (1.0) and C₇₀ (0.9 ± 0.15).^{1c,2a} By employing the relative actinometry method³⁹ using benzophenone as a reference ($\Phi_{\text{isc}} = 1.0$), we attempted to estimate the Φ_{isc} values of C₈₂. However, due to the quite weak signal of ³C₈₂*, an accurate value was not obtained. From a rough estimation, Φ_{isc} of C₈₂ was evaluated to be <0.01. The low Φ_{isc} value seems to be a common feature of higher fullerenes.

Reduction of C₈₂ in the Excited State. Irradiation of the 532 nm laser to a benzonitrile solution containing C₈₂ and TMPD excites C₈₂, mainly as mentioned above. At 50 ns after the laser irradiation, generation of ³C₈₂* was confirmed in the transient absorption spectrum (Figure 6). At 500 ns, new absorption bands appeared at 860, 720, and 600 nm, of which the first two absorption bands can be attributed to C₈₂*⁻ from the comparison with Figure 1, while the last one is due to TMPD*⁺.³⁵ The absorption–time profile at 860 nm (inset of Figure 6) can be divided into two components: the first is due to decay of ³C₈₂* and the second is due to C₈₂*⁻. Acceleration of the decay rate of ³C₈₂* in the presence of TMPD indicates generation of C₈₂*⁻ by photoinduced electron transfer via ³C₈₂* (eq 3). Triplet quenching rate of the reaction (k_{q}^{T}) was estimated



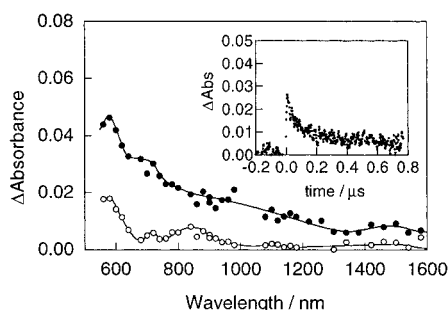
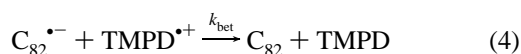


Figure 6. Transient absorption spectra of C_{82} (5.5×10^{-5} M) and TMPD (5.0×10^{-3} M) in benzonitrile at 50 ns (filled circles) and 500 ns (open circles) after the 532 nm laser irradiation. Inset: absorption-time profile at 860 nm.

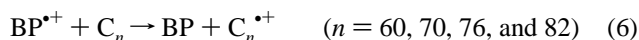
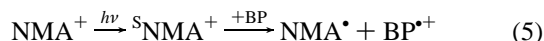
to be $2.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The estimated reaction rate constant was somewhat larger than that observed for the reaction of C_{76} and TMPD ($7.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$)¹¹ but was of the same order as those of C_{60} ($5.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) and C_{70} ($6.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$),^{2b} indicating the diffusion-limiting process.

Absorption-time profiles of the absorption bands of radical ions showed decay over several tens of microseconds. The observed decay of the radical ions can be attributed to the back-electron-transfer reaction (eq 4). By applying the second-order



plot to the absorption-time profile at 600 nm, which corresponds to the absorption band of $\text{TMPD}^{\bullet+}$, $k_{\text{bet}}/\epsilon = 9.6 \times 10^6 \text{ cm s}^{-1}$ was obtained, where k_{bet} is the back-electron transfer rate constant. Therefore, k_{bet} was estimated to be $5.8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ using ϵ of $\text{TMPD}^{\bullet+}$ ($6.0 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$),³⁵ indicating that the back-electron transfer is also the diffusion-limiting process.

Oxidation of C_{82} by Photosensitization. Nonell et al. reported that radical cation of C_{60} ($C_{60}^{\bullet+}$) was generated in high yield by a photosensitized electron-transfer reaction using a cosensitizer at high concentration.^{2c} Using NMA^+ and biphenyl (BP) as the sensitizer and the cosensitizer, respectively, $C_{60}^{\bullet+}$ was generated by the reaction schemes in eqs 5 and 6. Recently,



we reported that the same oxidation is also applicable to C_{70} and C_{76} .¹² Here, C_{82} was examined for this reaction. Immediately after 355 nm laser excitation, which excites NMA^+ mainly, a transient absorption band appeared at 680 nm, which can be attributed to $\text{BP}^{\bullet+}$ by eq 5 (Figure 7).^{12,40} With a decrease of the absorption band of $\text{BP}^{\bullet+}$, new absorption bands appeared at 980 and 840 nm at 2.5 μs after the laser excitation (inset of Figure 7). The new absorption bands can be attributed to $C_{82}^{\bullet+}$, indicating the electron-transfer reaction by eqs 5 and 6. From the change of observed decay-rate constant of $\text{BP}^{\bullet+}$, the reaction rate constant for eq 6 was estimated to be $1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, indicating effective radical ion formation as observed with other fullerenes (C_{60} , C_{70} , and C_{76}).^{2c,12}

Conclusion

Photophysical and photochemical properties of C_{82} were characterized by the laser flash photolysis method. Transient absorption bands of ${}^1C_{82}^*$ were quite weak, indicating low Φ_{isc}

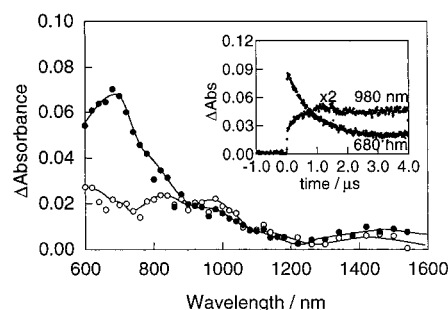


Figure 7. Transient absorption spectra of C_{82} (5.5×10^{-5} M), NMA^+ (1.8×10^{-4} M), and BP (2.2×10^{-1} M) in benzonitrile at 100 ns (filled circles) and 2.5 μs (open circles) after the 355 nm laser irradiation. Inset: absorption-time profiles at 980 and 680 nm.

(<0.01): low Φ_{isc} seems to be a common feature of higher fullerenes. Depending on size and symmetry, the HOMO-LUMO gap of higher fullerenes also becomes small, as indicated by the absorption spectrum. Because of the lower reduction potential compared to other fullerenes, C_{82} was reduced in the ground state by TMPD and DABCO, which are not very strong electron donors. Effective reactions at diffusion limiting rates were observed with photoinduced reduction and oxidation of C_{82} .

Acknowledgment. The present work is partly supported by the Grant-in-Aid on Scientific Research on Priority Area (B) on "Laser Chemistry of Single Nanometer Organic Particle" (No. 10207202) from the Ministry of Education, Science, Sports, and Culture, Japan.

Supporting Information Available: ^{13}C NMR of C_{82} (C_2) and an absorption spectrum of a mixture solution of C_{82} and TMPD are provided. This information is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) (a) Senssion, R. J.; Phillips, C. M.; Szarka, A. Z.; Romanow, W. J.; McGhie, A. R.; McCauley, J. P.; Smith, A. B.; Hochstrasser, R. M. *J. Phys. Chem.* **1991**, *95*, 6075. (b) Dimitrijevic, N. M.; Kamat, P. V. *J. Phys. Chem.* **1992**, *96*, 4811. (c) Palit, D. K.; Sapre, A. V.; Mittal, J. P.; Rao, C. N. R. *Chem. Phys. Lett.* **1992**, *195*, 1.
- (2) (a) Arbogast, J. W.; Foote, C. S. *J. Am. Chem. Soc.* **1991**, *113*, 8886. (b) Arbogast, J. W.; Foote, C. S.; Kao, M. *J. Am. Chem. Soc.* **1992**, *114*, 2277. (c) Nonell, S.; Arbogast, J. W.; Foote, C. S. *J. Phys. Chem.* **1992**, *96*, 4169. (d) Zhang, X.; Foote, C. S. *J. Am. Chem. Soc.* **1995**, *117*, 4271. (e) Zhang, X.; Fan, A.; Foote, C. S. *J. Org. Chem.* **1996**, *61*, 5465. (f) Bernstein, R.; Prat, F.; Foote, C. S. *J. Am. Chem. Soc.* **1999**, *121*, 464.
- (3) (a) Guldi, D. M.; Hungerbuhler, H.; Asmus, K.-D. *J. Phys. Chem.* **1995**, *99*, 9380. (b) Guldi, D. M.; Hungerbuhler, H.; Asmus, K.-D. *J. Phys. Chem.* **1995**, *99*, 13487. (c) Guldi, D. M.; Hungerbuhler, H.; Asmus, K.-D. *J. Phys. Chem. A* **1997**, *101*, 1783. (d) Guldi, D. M. *J. Phys. Chem. A* **1997**, *101*, 3895. (e) Thomas, K. G.; Biju, V.; George, M. V.; Guldi, D. M.; Kamat, P. V. *J. Phys. Chem. A* **1998**, *102*, 5341. (f) Guldi, D. M.; Torres-Garcia, G.; Mattay, J. *J. Phys. Chem. A* **1998**, *102*, 9679. (g) Guldi, D. M.; Hungerbuhler, H.; Asmus, K. D. *J. Phys. Chem. B* **1999**, *103*, 1444. (h) Polese, A.; Mondini, S.; Bianco, A.; Toniolo, C.; Scorrano, G.; Guldi, D. M.; Maggini, M. *J. Am. Chem. Soc.* **1999**, *121*, 3446.
- (4) (a) Biczok, L.; Linschitz, H.; Walter, R. I. *Chem. Phys. Lett.* **1992**, *195*, 339. (b) Sterein, C. A.; van Willigen, H.; Bizók, L.; Gupta, N.; Linschitz, H. *J. Phys. Chem.* **1996**, *100*, 8920. (c) Biczok, L.; Gupta, N.; Linschitz, H. *J. Am. Chem. Soc.* **1997**, *119*, 12601. (d) Gupta, N.; Linschitz, H.; Biczok, L. *Full. Sci. Technol.* **1997**, *5*, 343.
- (5) (a) Mikami, K.; Matsumoto, S.; Tono, T.; Suenobu, T.; Ishida, A.; Fukuzumi, S. *Synlett.* **1997**, 85. (b) Fukuzumi, S.; Suenobu, T.; Kawamura, S.; Ishida, A.; Mikami, K. *Chem. Commun.* **1997**, 291. (c) Fukuzumi, S. *Res. Chem. Int.* **1997**, *23*, 519. (d) Fukuzumi, S.; Suenobu, T.; Patz, M.; Hirasaka, T.; Itoh, S.; Fujitsuka, M.; Ito, O. *J. Am. Chem. Soc.* **1998**, *120*, 8060. (e) Fukuzumi, S.; Suenobu, T.; Fujitsuka, M.; Ito, O.; Tono, T.; Matsumoto, S.; Mikami, K. *J. Organomet. Chem.* **1999**, *574*, 32.

- (6) (a) Sasaki, Y.; Fujitsuka, M.; Watanabe, A.; Ito, O. *J. Chem. Soc., Faraday Trans.* **1997**, 93, 4275. (b) Nojiri, T.; Alam, M. M.; Konami, H.; Watanabe, A.; Ito, O. *J. Phys. Chem. A* **1997**, 101, 7943. (c) Nojiri, T.; Watanabe, A.; Ito, O. *J. Phys. Chem. A* **1998**, 102, 5215. (d) Alam, M. M.; Sato, M.; Watanabe, A.; Akasaka, T.; Ito, O. *J. Phys. Chem. A* **1998**, 102, 7447. (e) Luo, C. P.; Fujitsuka, M.; Huang, C. H.; Ito, O. *J. Phys. Chem. A* **1998**, 102, 8716. (f) El-Kemary, M.; Fujitsuka, M.; Ito, O. *J. Phys. Chem. A* **1999**, 103, 1329. (g) Akasaka, T.; Suzuki, T.; Maeda, Y.; Ara, M.; Wakahara, T.; Kobayashi, K.; Nagase, S.; Kako, M.; Nakadaira, Y.; Fujitsuka, M.; Ito, O. *J. Org. Chem.* **1999**, 64, 566.
- (7) Wang, Y. *Nature* **1992**, 356, 585.
- (8) Yoshino, K.; Xiao, H. Y.; Nuro, K.; Kiyomatsu, S.; Morita, S.; Zakikhov, A. A.; Noguchi, T.; Ohnishi, T. *Jpn. J. Appl. Phys.* **1993**, 32, L357.
- (9) Allemand, P.-K.; Khemani, K. C.; Koch, A.; Wudl, F.; Holczer, K.; Donovan, S.; Gruner, G.; Thompson, J. D. *Science* **1991**, 253, 301.
- (10) Hebard, A. F.; Rosseinsky, M. F.; Haddon, R. C.; Murphy, D. W.; Glarum, S. H.; Palstra, T. T. M.; Ramirez, A. P.; Kortan, A. R. *Nature* **1991**, 350, 600.
- (11) Fujitsuka, M.; Watanabe, A.; Ito, O.; Yamamoto, K.; Funasaka, H. *J. Phys. Chem. A* **1997**, 101, 4840.
- (12) Fujitsuka, M.; Watanabe, A.; Ito, O.; Yamamoto, K.; Funasaka, H. *J. Phys. Chem. A* **1997**, 101, 7960.
- (13) Guldi, D. M.; Liu, D.; Kamat, P. V. *J. Phys. Chem. A* **1997**, 101, 6195.
- (14) Bensasson, R. V.; Bienvenue, E.; Janot, J.-M.; Land, E. J.; Leach, S.; Seta, P. *Chem. Phys. Lett.* **1998**, 283, 221.
- (15) Guldi, D. M.; Asmus, K.-D. *J. Am. Chem. Soc.* **1997**, 119, 5744.
- (16) Terazima, M.; Hirota, N.; Shinohara, H.; Asato, K. *Electrochem. Soc. Proc.* **1995**, 95–10, 267.
- (17) Kamat, P. V.; Sauvé, G. *Electrochem. Soc. Proc.* **1995**, 95–10, 431.
- (18) Manolopoulos, D. M.; Fowler, P. W. *Chem. Phys. Lett.* **1991**, 187, 1.
- (19) Kikuchi, K.; Nakahara, N.; Wakabayashi, T.; Suzuki, S.; Shiromaru, H.; Miyake, Y.; Saito, K.; Ikemoto, I.; Kainosho, M.; Achiba, Y. *Nature* **1992**, 357, 142.
- (20) Achiba, K.; Kikuchi, K.; Aihara, Y.; Wakabayashi, T.; Miyake, Y.; Kainosho, M. *Mater. Res. Soc. Symp. Proc.* **1995**, 359, 3.
- (21) Akasaka, T.; Kato, T.; Kobayashi, K.; Nagase, S.; Yamamoto, K.; Funasaka, H.; Takahashi, T. *Nature* **1995**, 374, 600.
- (22) Akasaka, T.; Nagase, S.; Kobayashi, K.; Suzuki, T.; Kato, T.; Yamamoto, K.; Funasaka, H.; Takahashi, T. *J. Chem. Soc., Chem. Commun.* **1995**, 1343.
- (23) Suzuki, T.; Kikuchi, K.; Oguri, F.; Nakano, Y.; Suzuki, S.; Achiba, Y.; Yamamoto, K.; Funasaka, H.; Takahashi, T. *Tetrahedron* **1996**, 52, 4973.
- (24) Anderson, M. R.; Dorn, H. C.; Stevenson, S.; Burbank, P. M.; Gibson, J. R. *J. Am. Chem. Soc.* **1997**, 119, 437.
- (25) Yamamoto, K.; Funasaka, H.; Takahashi, T.; Akasaka, T. *J. Phys. Chem.* **1994**, 98, 2008.
- (26) Funasaka, H.; Sugiyama, K.; Yamamoto, K.; Takahashi, T. *J. Phys. Chem.* **1995**, 99, 1826.
- (27) Gebert, H.; Regenstein, W.; Bendig, J.; Kreysig, D. *Z. Phys. Chem.* **1982**, 263, 65.
- (28) Oxidation and reduction potentials of C₈₂ in benzonitrile were calculated from the reported redox potential difference between C₆₀ and C₈₂ in 1,2-dichlorobenzene²³ and the reduction potential of C₆₀ in benzonitrile.^{2b}
- (29) Kim, D.; Lee, M.; Suh, Y. D.; Kim, S. K. *J. Am. Chem. Soc.* **1992**, 114, 4, 4429.
- (30) Fujitsuka, M.; Luo, C. P.; Ito, O. *J. Phys. Chem. B* **1999**, 103, 334.
- (31) Kuwata, K.; Geske, D. *J. Am. Chem. Soc.* **1964**, 86, 2101.
- (32) Tanaka, K.; Zakikhov, A. A.; Yoshizawa, K.; Okahara, K.; Yamabe, T.; Kikuchi, K.; Suzuki, S.; Ikemoto, I.; Achiba, Y. *Solid State Commun.* **1993**, 85, 69.
- (33) Lawson, D. R.; Feldhein, D. L.; Foss, C. A.; Dorhout, P. K.; Elliot, C. M.; Martin, C. R.; Parkinson, B. *J. Phys. Chem.* **1992**, 96, 7175.
- (34) Guldi, D. M.; Hungerbuhler, H.; Janata, E.; Asmus, K.-D. *J. Phys. Chem.* **1993**, 97, 11258.
- (35) Hausser, K. H.; Murrell, J. N. *J. Chem. Phys.* **1957**, 27, 500.
- (36) Ausman, K. D.; Weisman, R. B. *Res. Chem. Intermed.* **1997**, 23, 431.
- (37) Arbogast, J. W.; Darmanyan, A. P.; Foote, C. S.; Rubin, Y.; Diederich, F. N.; Albarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Phys. Chem.* **1991**, 95, 11.
- (38) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973.
- (39) Carmichael, I.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1986**, 15, 1.
- (40) Shida, T. *Electronic Absorption Spectra of Radical Ions*; Elsevier: Amsterdam, 1988.