

Excited Triplet and Reduced Forms of C₈₄

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The triplet excited state behavior of C₈₄ has been probed by the triplet–triplet energy transfer method using pulse radiolytically generated biphenyl triplets in benzene. The triplet excited state has a weak absorption in the UV (difference absorption maxima at 310 and 345 nm) but no significant absorption in the visible. The rate constants for energy transfer from ³BP* and ³C₆₀* are 4×10^9 and $4.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, respectively. Triplet excited state properties of ³C₈₄* are compared with other fullerenes. A photocatalytic method has also been successfully employed to reduce C₈₄ in a UV-irradiated colloidal TiO₂ suspension.

Introduction

The photophysical, photochemical, and photoelectrochemical properties of fullerenes, C₆₀ and C₇₀, have been studied extensively over the past couple of years [see, for example, refs 1–26]. The long-lived triplet excited state and absorption in the visible makes fullerenes suitable for photosensitization, singlet oxygen production, and solar energy conversion. Doped polymer films have also been shown to possess photoconductive properties. There is now increasing interest in studying the physical properties of larger fullerenes, C₇₆, C₇₈, C₈₂, C₈₄, etc.^{27–31} However, little is known regarding the excited state behavior of these larger fullerenes.

C₈₄ is one of the larger fullerenes produced in abundant quantities during the synthesis of C₆₀. Unlike C₆₀ and C₇₀, C₈₄ exists in two isomers, D₂ and D_{2d}, in the ratio 2:1.^{27,28} The visible absorption spectra of C₈₄²⁹ and the reduction potentials of C₈₄^{27–31} have already been reported. At least six reversible reductions have been characterized using cyclic voltammetry.^{27a,b} Although distinctively different electronic properties of these two isomers were observed in electrochemical and ESR studies, the separation of the two isomers of C₈₄ has not yet been achieved. Consequently, a mixture of the two isomers has been used in this investigation. We report here, for the first time, experimental results which characterize triplet excited state properties of C₈₄. We also report the photoelectrochemical reduction of C₈₄ in colloidal TiO₂ suspension.

Experimental Section

Materials. Mass-pure C₈₄ was obtained via selective solvent extraction followed by HPLC chromatography with a semi-preparative Buckyclutcher column (Regis) run in recycling mode. Details of the selective solvent enrichment techniques will be published later.^{26a} The purity of the sample was checked by surface analysis via laser ionization (SALI) mass spectrometry (MS), a technique that has been used extensively at SRI International for analysis of fullerene samples.^{27b} SALI-MS showed that the fullerene purity exceeded 99.5%, with the only impurity peaks belonging to C₈₂ and C₈₆; in particular, no C₆₀ or C₇₀ was present in the SALI-MS spectrum obtained. The

sample was washed with diethyl ether three times and then dried for a period of 48 h in a vacuum oven held at 343 K.

Optical Measurements. Absorption spectra were recorded with a Perkin-Elmer 3840 diode array spectrophotometer. Nanosecond laser flash photolysis experiments were carried out with a Laser Photonics PRA/Model UV-24 nitrogen laser system (337 nm, 2 ns pulse width, 2–4 mJ/pulse) with a front face excitation geometry. A typical experiment consisted of a series of 2–3 replicate shots per single measurement. The average signal was processed with an LSI-11 microprocessor interfaced with VAX-3400 computer. Details of the experimental setup can be found elsewhere.^{32a}

Pulse radiolysis experiments were performed at 296 K with the Notre Dame 7 MeV ARCO LP-7 linear accelerator, the operating conditions of which are described elsewhere.^{32b} The dose per pulse was in the range 1–5 Gy, determined by thiocyanate dosimetry. The solutions were saturated with nitrogen or oxygen and flowed continuously during the experiment.

Results and Discussion

The absorption spectrum of C₈₄ in toluene is compared to that of C₆₀ in Figure 1. While the solution of C₆₀ is purple, the solutions of C₈₄ exhibit yellow-green color. The C₈₄ exhibits significantly stronger absorption in the visible. The details of the structural and electronic properties of the C₈₄ are presented elsewhere.²⁹ Direct excitation of C₈₄ via nanosecond laser flash photolysis using 337 nm excitation wavelength (2 mJ/pulse) did not yield a conclusive spectrum of ³C₈₄*; the transient absorbance in the UV–visible region was very low (<0.002).³³ This observation indicates that either the intersystem crossing efficiency for the ³C₈₄* generation is very low or the triplet excited state has a very low extinction coefficient in the UV–visible region. An alternate route of triplet–triplet energy transfer was therefore employed to generate ³C₈₄*.

Pulse Radiolysis Experiments. Radiolysis of a benzene solution containing a high concentration of biphenyl is known to yield relatively long-lived excited biphenyl triplet with absorption maximum at 360 nm. The resulting biphenyl triplets are capable of transferring energy to a molecule with a lower triplet energy. This technique has been successfully used by us and others to generate ³C₆₀* and ³C₇₀*.^{6a,9,10} The absorbed doses were in the range 4–20 Gy/pulse. The experiments were carried out with a continuous flow of the sample solution.

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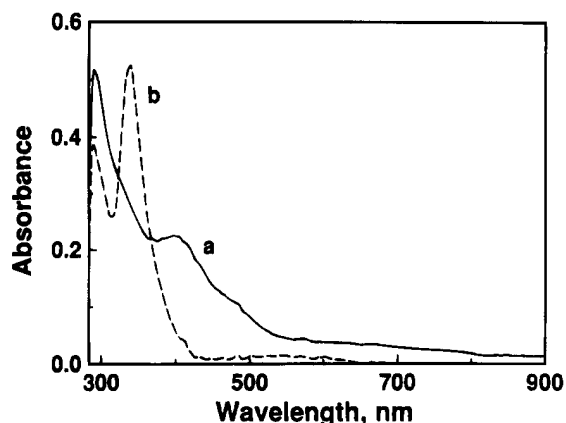


Figure 1. Absorption spectra of (a) 10 μM C₈₄ and (b) 6.5 μM C₆₀ in toluene.

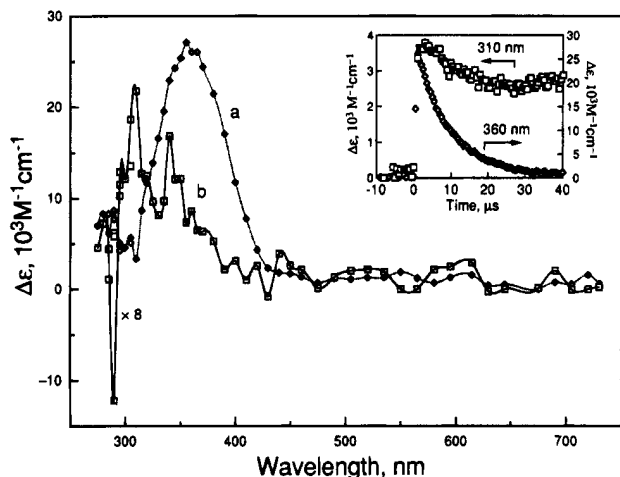
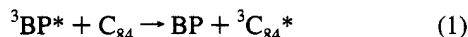


Figure 2. Transient absorption spectra obtained (a) 1 μs (³BP*) and (b) 35 μs (³C₈₄*) after pulse radiolysis of deaerated benzene solution containing 0.05 M biphenyl and 10 μM C₈₄. Inset shows normalized decay traces recorded at 360 and 310 nm corresponding to the transients ³BP* and ³C₈₄*, respectively.

The biphenyl triplet is relatively short-lived in the presence of C₈₄ as a result of the T–T energy transfer process (reaction 1).



The bimolecular rate constant for the quenching of biphenyl triplet by C₈₄ was $4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. This value, which is close to a diffusion-controlled process, is slightly lower than the values of 1.7×10^{10} and $2.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for energy transfer to C₆₀ and C₇₀, respectively.^{6a} In the absence of C₈₄, ³BP* is the only species generated in the pulse radiolysis experiment. However, in the presence of C₈₄, transients with two different lifetimes were evident. This is clearly evident from the absorption–time profiles recorded in the presence of C₈₄ (inset in Figure 2).

The transient absorption spectra obtained after 1 and 35 μs are shown in Figure 2. While the transient absorption spectrum recorded at short times (spectrum a) corresponds to ³BP*, the transient absorption spectrum recorded at longer times (spectrum b) corresponds to ³C₈₄*. The difference absorption spectrum of ³C₈₄* exhibits maxima at 310 and 345 nm. The maximum bleaching observed at 290 nm corresponds to the ground state maximum in this region. It has been shown earlier that ³C₆₀* has significant absorptions in the visible,^{1–10} but surprisingly, ³C₈₄* does not exhibit any noticeable absorption in the visible

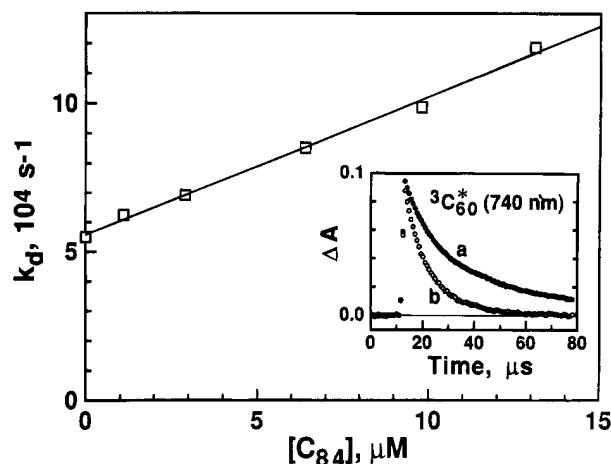


Figure 3. Dependence of pseudo-first-order decay rate constant of ³C₆₀* on the concentration of C₈₄. Inset shows the decay of ³C₆₀* at 740 nm: (a) in the absence and (b) in the presence of 135 μM C₈₄.

TABLE 1: Triplet Excited State Properties of Fullerenes

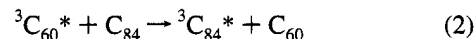
	C ₆₀ ^a	C ₇₀ ^a	C ₈₄ ^b
abs max, nm	400, 740	435, 970	310
extinction coefficient, M ⁻¹ cm ⁻¹	6600, 16000	9000, 4000	4430
lifetime, μs	250	250	<100
<i>k</i> (³ C ₆₀ *), ^c 10 ⁹ M ⁻¹ s ⁻¹	0.2	2.4	4.7

^a In benzene or toluene (compiled from refs, 6a, 10b, 11a, and 12b).

^b In benzene (present study). ^c Bimolecular rate constant for the quenching of ³C₆₀* by the corresponding fullerene.

region. By using the expression for energy transfer method,³⁴ we estimate the maximum extinction coefficient of ³C₈₄* at 310 nm to be 4430 M⁻¹ cm⁻¹. (The value of 27 100 M⁻¹ cm⁻¹ was used as ϵ_d for ³BP* at 360 nm.)³⁴

Energy Transfer between ³C₆₀* and C₈₄. Triplet–triplet energy transfer between ³C₆₀* and C₈₄ was probed by laser flash photolysis. The absorption–time profiles of ³C₆₀* at 740 nm recorded in the presence and absence of C₈₄ (inset of Figure 3) show that C₈₄ is able to quench the triplet excited state of C₆₀ via T–T energy transfer process (reaction 2).

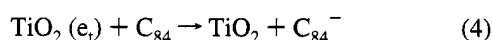
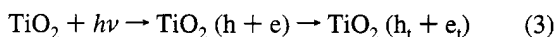


The quenching of ³C₆₀* by C₈₄ was monitored from the absorption decay at 740 nm by varying the concentration of C₆₀. The dependence of the pseudo-first-order rate constant of ³C₆₀* decay on the C₈₄ concentration is shown in Figure 3. The bimolecular rate constant for the quenching of ³C₆₀* by C₈₄ determined from the slope of this plot is $4.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. This value is similar to the one reported for the quenching of ³C₆₀* by C₇₀ ($2.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$).^{12b} The nearly diffusion-controlled quenching rate constant observed in the present set of experiments suggests that the triplet energy of C₈₄ is lower than that of ³C₆₀*. Strong ground state absorption of C₆₀ and C₈₄ and weak absorption of ³C₈₄* limited the resolution of transient absorption measurements in the UV region.

Comparison of ³C₈₄* Properties with Other Fullerenes. The absorption properties of ³C₈₄* are compared with other fullerene triplets in Table 1. The only spectral features in the difference absorption spectrum of ³C₈₄* that are prominent are the absorption bands at 310 and 345 nm. The absence of a major absorption band of triplet excited C₈₄ in the visible suggests a close match between the ground and excited state spectra. Of all the fullerenes that have been investigated to date, only triplet C₆₀ is known to exhibit a prominent 740 nm absorption band with a significantly higher extinction coefficient

of $14\,000\text{ M}^{-1}\text{ cm}^{-1}$.^{11a} However, triplet C_{70} exhibits relatively weak absorption bands in the visible. These observations suggest that visible absorption bands are less prominent for triplet excited states of higher fullerenes. However, all of these excited fullerenes are long-lived with intrinsic decay lifetimes greater than $100\ \mu\text{s}$. Self-quenching processes such as T-T annihilation and ground state quenching often accelerate the deactivation of the triplet excited state. Another interesting aspect involves energy transfer between two different fullerene molecules. The bimolecular rate constant for the quenching of ${}^3C_{60}^*$ by a fullerene molecule increases with increasing number of carbon atoms in the unexcited fullerene molecule (Table 1). If we attribute this increase in the quenching rate constant to the increasing energy gap between the donor and acceptor triplets, it is evident that larger fullerenes have lower triplet energies. A decrease in the energy of the lowest unoccupied molecular orbitals of the fullerenes has also been observed in the electrochemical reduction of larger fullerenes.^{27c}

Reduction of C_{84} in Colloidal TiO_2 Suspension. Controlled reduction of fullerenes has also been a topic of immense interest in recent years. Up to six reversible reductions have been reported for C_{84} .^{27b,31} We have now employed a photoelectrochemical approach to reduce C_{84} in preirradiated colloidal TiO_2 suspension (reactions 3 and 4).



The ability of semiconductor clusters to carry out controlled one-electron reduction of C_{60} and C_{70} under UV excitation has been demonstrated earlier.^{35,36} The semiconductor TiO_2 should be an excellent choice to carry out one-electron reduction of C_{84} since the energy of its conduction bands ($E_{CB} = -0.5\text{ V}$ vs NHE at pH 7) thermodynamically favors one-electron reduction ($E^0(C_{84}/C_{84}^-) \approx -0.08\text{ V}$ vs NHE).

A deaerated suspension of colloidal TiO_2 (10 mM) in 50/50 toluene/ethanol was preirradiated with a 1000 W xenon/mercury lamp to induce charge separation followed by trapping of holes (h_t) and electrons (e_t) within the semiconductor colloids (reaction 3). The solution turned blue as the UV irradiation was continued for 3–5 min. This blue coloration of the colloidal suspension is a characteristic feature of trapped electrons in TiO_2 colloids.³⁶ An aliquot (40 μL) of deaerated C_{84} solution in toluene ($2 \times 10^{-4}\text{ M}$) was then added to both sample and reference cells (total volume 1 mL). Absorption spectra recorded before and after the addition of C_{84} are shown in Figure 4. A cell containing only 50/50 toluene/ethanol solvent mixture was used as the reference. The spectrum recorded after the addition of C_{84} (spectrum b in Figure 4) shows a decreased absorption at 700 nm and an increased absorption around 330 nm. The decrease in the absorption at 330 nm indicates that the trapped electrons are scavenged by C_{84} to produce C_{84}^- (reaction 3). It should be noted that the trapped electrons in a preirradiated TiO_2 suspension are relatively long-lived and do not disappear without the addition of C_{84} .

The spectral features of C_{84}^- were further probed by subtracting the contribution of TiO_2 absorption to the overall spectrum. The difference absorption spectra recorded after each incremental addition of C_{84} solution show increased absorption at 330 nm with increasing C_{84} concentration (inset of Figure 4). Bleaching around 300 nm further confirms the disappearance of C_{84} to form C_{84}^- . The disappearance of C_{84} cannot be attributed to direct photolysis of C_{84} since the TiO_2 suspension was irradiated with UV light before the addition of C_{84} . These observations demonstrate the feasibility of carrying out one-

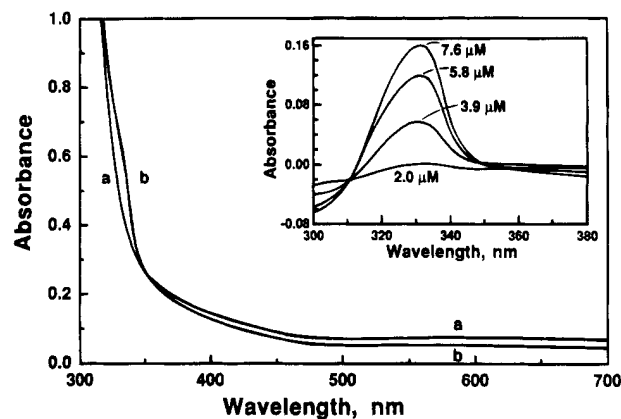


Figure 4. Absorption spectra of 10 mM TiO_2 colloidal in 50/50 toluene/ethanol (path length = 2 mm, volume = 1 mL) (a) after UV illumination for 3 min and (b) after addition of C_{84} to the preirradiated TiO_2 suspension ($[C_{84}] = 7.6\ \mu\text{M}$). Inset shows the difference absorption spectra of C_{84}^- . The spectra were recorded following the addition of various amounts of C_{84} and corrected for the absorbance of TiO_2 colloids.

electron reduction of C_{84} with semiconductor colloids. Further experiments are underway to explore the role of excited C_{84} in its participation in the photochemical reactions.

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References and Notes

- (1) (a) Arbogast, J. W.; Darmanyan, A. P.; Foote, C. S.; Rubin, Y.; Diedrich, F. N.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Phys. Chem.* **1991**, *95*, 11. (b) Arbogast, J. W.; Foote, C. S. *J. Am. Chem. Soc.* **1991**, *113*, 8886. (c) Foote, C. S. *Top. Curr. Chem.* **1994**, *169*, 301.
- (2) (a) Ebbesen, T. W.; Tanigaki, K.; Kuroshima, S. *Chem. Phys. Lett.* **1991**, *181*, 501. (b) Tanigaki, K.; Ebbesen, T. W.; Kuroshima, S. *Chem. Phys. Lett.* **1991**, *185*, 189.
- (3) Wasielewski, M. R.; O'Neil, M. P.; Lykke, K. R.; Pellin, M. J.; Gruen, D. M. *J. Am. Chem. Soc.* **1991**, *113*, 2774.
- (4) (a) Senison, R. J.; Phillips, C. M.; Szarka, A. Z.; Romanow, W. J.; McGhie, A. R.; McCauley, Jr., J. P.; Smith, A. B.; Hochstrasser, R. M. *J. Phys. Chem.* **1991**, *95*, 6075. (b) Senison, R. J.; Szarka, A. Z.; Smith, G. R.; Hochstrasser, R. M. *Chem. Phys. Lett.* **1991**, *185*, 179.
- (5) (a) Hung, R. R.; Grabowski, J. J. *J. Phys. Chem.* **1991**, *95*, 6073. (b) Hung, R. R.; Grabowski, J. J. *Chem. Phys. Lett.* **1992**, *192*, 249.
- (6) (a) Dimitrijevi, N. M.; Kamat, P. V. *J. Phys. Chem.* **1992**, *96*, 4811. (b) Gevaert, M.; Kamat, P. V. *J. Phys. Chem.* **1992**, *96*, 9863. (d) Samanta, A.; Kamat, P. V. *Chem. Phys. Lett.* **1992**, *199*, 635.
- (7) Kajii, Y.; Nakagawa, T.; Suzuki, S.; Achiba, Y.; Obi, K.; Shbuya, K. *Chem. Phys. Lett.* **1991**, *181*, 100.
- (8) (a) Terazima, M.; Hirota, N.; Shinohara, H.; Saito, Y. *J. Phys. Chem.* **1991**, *95*, 6490. (b) Terazima, M.; Sakurada, K.; Hirota, N.; Shinohara, H.; Saito, Y. *J. Phys. Chem.* **1993**, *97*, 5447.
- (9) (a) Palit, D. K.; Sapre, A. V.; Mittal, J. P. *Indian J. Chem., Sect. A* **1992**, *31*, F46. (b) Palit, D. K.; Sapre, A. V.; Mittal, J. P.; Rao, C. N. R. *Chem. Phys. Lett.* **1992**, *195*, 1. (c) Palit, D. K.; Ghosh, H. N.; Pal, H.; Sapre, A. V.; Mittal, J. P.; Seshadri, R.; Rao, C. N. R. *Chem. Phys. Lett.* **1992**, *198*, 113. (d) Ghosh, H. N.; Pal, H.; Sapre, A. V.; Mittal, J. P. *J. Am. Chem. Soc.* **1993**, *115*, 11722.
- (10) (a) Bensasson, R. V.; Hill, T.; Lambert, C.; Land, E. J.; Leach, S.; Truscott, T. G. *Chem. Phys. Lett.* **1993**, *201*, 326. (b) Bensasson, R. B.; Hill, T.; Lambert, C.; Land, E. J.; Leach, S.; Truscott, T. G. *Chem. Phys. Lett.* **1993**, *206*, 197.
- (11) (a) Biczok, L.; Linschitz, H.; Walter, R. I. *Chem. Phys. Lett.* **1992**, *195*, 339. (b) Zeng, Y.; Biczok, L.; Linschitz, H. *J. Phys. Chem.* **1992**, *96*, 5237. (c) Steren, C. A.; Levsten, P. R.; Van Willigen, H.; Linschitz, H.; Biczok, L. *Chem. Phys. Lett.* **1993**, *204*, 23.
- (12) (a) Sibley, S. P.; Argentine, S. M.; Francis, A. H. *Chem. Phys. Lett.* **1992**, *188*, 187. (b) Fraelich, M. R.; Weisman, R. B. *J. Phys. Chem.* **1993**, *97*, 11145. (c) Nadochenko, V. A.; Vasil'ev, I. V.; Denisov, N. N.; Rubtsov, I. V.; Lobach, A. S.; Moravskii, A. P.; Shestakov, A. F. *J.*

Photochem. Photobiol. A: Chem. **1993**, *70*, 153. (d) Haynes, D. R.; Tokmakoff, A.; George, S. M. *Chem. Phys. Lett.* **1993**, *214*, 50.

(13) Miller, B.; Rosamilia, J. M.; Dabbagh, G.; Tycko, R.; Haddon, R. C.; Muller, A. J.; Wilson, W.; Murphy, D. W.; Hebard, A. F. *J. Am. Chem. Soc.* **191**, *113*, 6291.

(14) (a) Wang, Y.; Cheng, L.-T. *J. Phys. Chem.* **1992**, *96*, 1530. (b) Wang, Y. *J. Phys. Chem.* **1992**, *96*, 764. (c) Talapatra, G. B.; Manickam, N.; Samoc, M.; Orczyk, M. E.; Karna, S. P.; Prasad, P. N. *J. Phys. Chem.* **1992**, *96*, 5206.

(15) Allemand P.-M.; Koch, A.; Wudl, F.; Rubin, Y.; Diederich, F.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Am. Chem. Soc.* **1990**, *113*, 1050.

(16) (a) Dubois, D.; Kadish, K. M.; Flanagan, S.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 7773. (b) Dubois, D.; Kadish, K. M.; Flanagan, S.; Haufler, R. E.; Chibante, L. P. F.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 4364. (c) Dubois, D.; Moninot, G.; Wlodzimierz, K.; Thomas Jones, M.; Kadish, K. M. *J. Phys. Chem.* **1992**, *96*, 7137.

(17) Xie, Q.; Perez-Cordero, E.; Echegoyen, L. *J. Am. Chem. Soc.* **1992**, *114*, 3978.

(18) (a) Jehoulet, C.; Bard, A. J.; Wudl, F. *J. Am. Chem. Soc.* **1991**, *113*, 5456. (b) Zhou, F.; Yau, S.-L.; Jehoulet, C.; Laude, D. A., Jr.; Guan, Z.; Bard, A. J. *J. Phys. Chem.* **1992**, *96*, 4160.

(19) (a) Lawson, D. R.; Feldheim, D. L.; Foss, C. A.; Dorhout, P.; Elliot, C. M.; Martin, C. R.; Parkinson, B. *J. Electrochem. Soc.* **1992**, *139*, L68. (b) Lawson, D. R.; Feldheim, D. L.; Foss, C. A.; Dorhout, P.; Elliot, C. M.; Martin, C. R.; Parkinson, B. *J. Phys. Chem.* **1992**, *96*, 7175.

(20) Arbogast J. W.; Foote, C. S.; Kao, M. *J. Am. Chem. Soc.* **1992**, *114*, 2277.

(21) (a) Sariciftci, N. S.; Smilowitz, L.; Heeger, A. J.; Wudl, F. *Science* **1992**, *258*, 1474. (b) Hwang, K. C.; Mauzerall, D. *J. Am. Chem. Soc.* **1992**, *114*, 9705.

(22) Kato, T.; Kodama, T.; Shida, T.; Nakagawa, T.; Matsui, Y.; Suzuki, S.; Shiromaru, H.; Yamauchi, K.; Achiba, Y. *Chem. Phys. Lett.* **1991**, *180*, 446.

(23) Dimitrijevic, N. M.; Kamat, P. V. *J. Phys. Chem.* **1993**, *97*, 7623.

(24) (a) Guldi, D. M.; Hungerbühler, H.; Janata, E.; Asmus, K.-D. *J. Phys. Chem.* **1993**, *97*, 11258. (b) Guldi, D. M.; Hungerbühler, H.; Janata, E.; Asmus, K.-D. *J. Chem. Soc., Chem. Commun.* **1993**, 84. (c) Hungerbühler, H.; Guldi, D. M.; Asmus, K. D. *J. Am. Chem. Soc.* **1993**, *115*, 3386. (d) Guldi, D. M.; Hungerbühler, Wilhelm, M.; Asmus, K.-D. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1391. (e) Guldi, D. M.; Neta, P.; Asmus, K.-D. *J. Phys. Chem.* **1994**, *98*, 4617. (f) Guldi, D. M.; Huie, R.; Neta, P.; Hungerbühler, H.; Asmus, K.-D. *Chem. Phys. Lett.* **1994**, *223*, 511.

(25) (a) Schell-Sorokin, A. J.; Mehran, F.; Eaton, G. R.; Eaton, S. S.; Viehbeck, A.; O'Toole, T. R.; Brown, C. A. *Chem. Phys. Lett.* **1992**, *195*, 225. (b) Bhyrappa, P.; Paul, P.; Stinchcombe, J.; Boyd, P. D. W.; Reed, C. A. *J. Am. Chem. Soc.* **1993**, *115*, 11004.

(26) (a) Dimitrijevic, N. M. *Chem. Phys. Lett.* **1992**, *194*, 457. (b) Dimitrijevic, N. M.; Fessenden, R. W.; Kamat, P. V. *J. Phys. Chem.* **1993**, *97*, 615.

(27) (a) Boulas, P.; Jones, M. T.; Kadish, K. M.; Ruoff, R. S.; Lorents, D. C.; Malhotra, R.; Tse, D. S. In *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K. M., Ruoff, R. S., Eds.; The Electrochemical Society: Pennington, NJ, 1994; Vol. 94-24, p 1007. (b) Boulas, P.; Jones, M. T.; Kadish, K. M.; Ruoff, R. S.; Lorents, D. C.; Tse, D. S. In *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K. M., Ruoff, R. S., Eds.; The Electrochemical Society: Pennington, NJ, 1994; Vol. 94-24, p 995. (c) Selegue, J. P.; Shaw, J. P.; Guarr, T. F.; Meier, M. S. In *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K. M., Ruoff, R. S., Eds.; The Electrochemical Society: Pennington, NJ, 1994; Vol. 94-24, p 1274. (d) Moro, L.; Ruoff, R. S.; Becker, C. H.; Lorents, D. L.; Malhotra, R. *J. Phys. Chem.* **1993**, *97*, 6801-6805 and references therein.

(28) Manolopoulos, D. E.; Fowler, P. W. *J. Chem. Phys.* **1992**, *96*, 7603.

(29) Wang, X.-Q.; Wang, C. Z.; Zhang, B. L.; Ho, K. M. *Phys. Rev. Lett.* **1992**, *69*, 69.

(30) Kikuchi, K.; Nakahara, N.; Honda, M.; Suzuki, S.; Saito, K.; Shiromaru, H.; Yamauchi, K.; Ikemoto, I.; Kuramochi, T.; Hino, S.; Achiba, Y. *Chem. Lett.* **1991**, 1607-1610.

(31) Meier, M. S.; Guarr, T. F.; Selegue, J. P.; Vance, V. K. *J. Chem. Soc., Chem. Commun.* **1993**, 63.

(32) (a) Nagarajan, V.; Fessenden, R. W. *J. Phys. Chem.* **1985**, *89*, 2330. (b) Patterson, L. K.; Lilie, J. *Int. J. Radiat. Phys. Chem.* **1974**, *6*, 129.

(33) A caution regarding the contribution from organic impurities that might have associated with C₈₄ during the extraction/separation process: When a commercially obtained sample of C₈₄ was excited with 308 nm laser pulse, two different transients with absorption maxima at 445 and 350 nm were observed. These absorption peaks disappeared when the excitation wavelength was changed to 337 nm.

(34) Carmichael, I.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1.

(35) Kamat, P. V. *J. Am. Chem. Soc.* **1991**, *113*, 9705.

(36) Kamat, P. V.; Bedja, I.; Hotchandani, S. *J. Phys. Chem.* **1994**, *98*, 9137.

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