# Capped Fullerenes: Stabilization of Water-Soluble Fullerene Monomers As Studied by Flash Photolysis and Pulse Radiolysis

**Dirk M. Guldi**

*Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556*

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Functionalization of $C_{60}$ with hydrophilic groups promotes the water solubility of the fullerene core which leads in aqueous solution to the irreversible formation of clusters. Capping the surface of water-soluble fullerene derivatives with surfactants (cetyltrimethylammonium chloride or Triton X-100) was found to exclude formation of fullerene clusters and, in turn, to stabilize fullerene monomers. Flash photolytic and pulse radiolytic techniques were employed to generated excited and reduced states of fullerene monomers and fullerene clusters **1**−**3**. Fullerene aggregation was found to have no significant effects on the physicochemical properties related to the generation and lifetime of the excited singlet state. Nanosecond studies of the processes following photoexcitation revealed noticeable differences between monomeric and colloidal derivatives **1**−**3** for the absorption maximum of the corresponding $^*T_1 \rightarrow {}^*T_n$ absorptions. Clustering was found to invoke also remarkable changes for the decay of the fullerene's excited triplet state. Similarly, $\lambda_{max}$ of the $\pi$-radical anions **1**−**3** is very sensitive to the environmental parameters of the accommodating assembly. In surfactant media, the maxima ($[(C_{60}{}^{\bullet -})(C_4H_{10}N^+)]_{surfactant}$ 1010 nm) were generally blue-shifted relative to the analogous $\gamma$-CD complexes ($[(C_{60}{}^{\bullet -})(C_4H_{10}N^+)]/\gamma$-CD 1030 nm). On the basis of comparison with fullerene clusters and $\gamma$-CD-incorporated complexes, evidence was found that suggests the presence of fullerene monomers in a core(fullerene)−shell(surfactant) type structure.

## 1. Introduction

The unique symmetrical shape, the large size of its $\pi$-system, and characteristic physicochemical properties, such as facile reduction[1,2] and photosensitization,[3,4] of buckminsterfullerene raised the expectation that $C_{60}$ plays an active role in biologically relevant processes. The predominant hydrophobic character of this spherical carbon allotrope, however, hampers solubilization in polar media, including water. A successful strategy to improve this difficulty requires the design of water-soluble fullerene derivatives. Thus, functionalization of $C_{60}$ with hydrophilic addends has become a central topic in synthetic fullerene chemistry.[5−7]

Fullerenes ($C_{60}$, $C_{70}$, etc.) are susceptible for accepting multiple electrons in reversible one-electron steps.[8] This leads to the generation of stable radical anions which can be conveniently studied by radiolytic techniques.[9−11] However, lowering the fullerene's hydrophobic surface via covalent functionalization has been found to have a substantial impact on the electron acceptor properties. The reduction potentials, as determined by cyclic voltammetry, shift gradually to more cathodic potentials with increasing degree of functionalization.[12−15] In turn, the reactivity of functionalized fullerene derivatives toward electron transfer from strongly reducing species such as hydrated electrons and $(CH_3)_2{}^{\bullet}C(OH)$ reveals a noticeable slowdown relative to pristine $C_{60}$.[16]

Although attachment of only a single hydrophilic addend promotes the water solubility,[17] strong adsorption forces between the fullerene cores lead to the instantaneous and irreversible formation of clusters.[18] As a consequence of this aggregation, the lifetime of the excited triplet state is reduced by orders of magnitude, and detectable reduction is limited to fullerene monomers. On the other hand, increasing the number of addends at the fullerene core, e.g. via controlled bis-, tris-, or even polyfunctionalization ($C_{60}(OH)_{18}$−$C_{60}(OH)_{22}$), and thereby lowering the fullerene's hydrophobic surface, prevents formation of colloidal $C_{60}$ clusters.[16]

The reactivity of colloidal $C_{60}$ clusters toward electron transfer depends strongly on the surface modification. For example, monoderivatives that bear negatively charged carboxylic groups, in particular $C_{60}C(COO^-)_2$ **1** and $C_{60}(C_9H_{11}O_2)(COO^-)$ **2**, showed no noticeable reduction of the fullerene cores.[16,18] In contrast, the presence of a quartery ammonium cation in $C_{60}$-$(C_4H_{10}N^+)$ **3**, besides promoting the water solubility, facilitates the reduction of the fullerene core, even relative to pristine $C_{60}$.[11]

Surfactants, in particular Triton X-100 and BRIJ 35, have been successfully employed to solubilize pristine $C_{60}$ in aqueous media in reasonable yields.[19−23] Although derivatives **1**−**3** are quite soluble in water, in the present investigation utilization of cationic (cetyltrimethylammonium chloride) and nonionic (Triton X-100) detergents will be shown to be crucial to cap the fullerene core and, thus, obstruct formation of colloidal fullerene clusters.

## 2. Experimental Section

Details of the synthesis of **1** and **3** (see for structural details Figure 1) are described in earlier contributions.[17] Derivative **2** was purchased from MER Corporation (Tuscon, AZ). 1,4-Diazabicyclo[2.2.2]octane (DABCO), cetyltrimethylammonium chloride, Triton X-100, and $\gamma$-cyclodextrin were purchased from Aldrich. All organic solvents were redistilled before use. Fullerene complexes with $\gamma$-cyclodextrin were prepared according to a previously described procedure.[24]

Absorption spectra were recorded with a Milton Roy Spectronic 3000 Array spectrophotometer. Picosecond laser flash photolysis experiments were carried out with 355 nm laser pulses from a mode-locked, Q-switched Quantel YG-501 DP Nd:YAG laser system (pulse width 18 ps, 2−3 mJ/pulse). Nanosecond experiments were performed with laser pulses from a Quanta-Ray CDR Nd:YAG system (355 nm, 6 ns pulse width, 5−10 mJ/pulse) or from a Molectron UV-400 nitrogen laser

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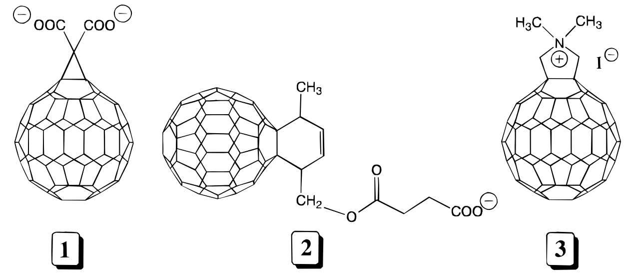

**Figure 1.** Functionalized fullerene derivatives used in this study.

system (337 nm, 8 ns pulse width, 1 mJ/pulse) in a front face excitation geometry.[25] Pulse radiolysis experiments were performed by utilizing 50 ns pulses of 8 MeV electrons from a Model TB-8/16-1S Electron Linear Accelerator. Basic details of the equipment and the data analysis have been described elsewhere.[26] Dosimetry was based on the oxidation of $SCN^-$ to $(SCN)_2^{\bullet -}$, which in $N_2O$-saturated aqueous solutions takes place with $G \sim 6$ ($G$ denotes the number of species per 100 eV, or the approximate micromolar concentration per 10 J of absorbed energy). The radical concentration generated per pulse amounts to $(1-3) \times 10^{-6}$ M for all the systems investigated in this study.

**Radiolytic Reduction.** Radiolytic reduction of fullerene solutions were conducted in either $N_2$- or $N_2O$-saturated, dilute aqueous solution containing 10 vol % 2-propanol. Under these experimental conditions the reactive radical species ${}^{\bullet}H$, ${}^{\bullet}OH$, $e_{aq}^-$ are produced in addition to the molecular products ($H_2$, $H_2O_2$) and $H_{aq}^+$.

$$H_2O \xrightarrow{\text{radiolysis}} {}^{\bullet}H, {}^{\bullet}OH, e_{aq}^-, H_{aq}^+, H_2, H_2O_2 \qquad (1)$$

Reaction of the ${}^{\bullet}OH$ and ${}^{\bullet}H$ radicals with 2-propanol leads to conversion into the reducing radical species ($(CH_3)_2{}^{\bullet}C(OH)$).

$$(CH_3)_2CH(OH) + {}^{\bullet}OH\ ({}^{\bullet}H) \rightarrow (CH_3)_2{}^{\bullet}C(OH) + H_2O\ (H_2) \qquad (2)$$

The strongly reducing $(CH_3)_2{}^{\bullet}C(OH)$ radicals ($E_o = -1.39$ V versus NHE)[27] are then expected to transfer an electron to the fullerene core.

$$C_{60}C(COO^-)_2 + (CH_3)_2{}^{\bullet}C(OH) \rightarrow (C_{60}{}^{\bullet -})C(COO^-)_2 + (CH_3)_2CO + H^+ \qquad (3)$$

Under $N_2$-saturated conditions the hydrated electrons may directly reduce the fullerene via

$$C_{60}C(COO^-)_2 + e_{aq}^- \rightarrow (C_{60}{}^{\bullet -})C(COO^-)_2 \qquad (4)$$

while in $N_2O$-purged solutions they are converted to hydroxyl radicals and, subsequently, to $(CH_3)_2{}^{\bullet}C(OH)$.

$$e_{aq}^- + N_2O \rightarrow N_2 + O^{\bullet -} \qquad (5)$$

$$O^{\bullet -} + H_2O \rightarrow {}^{\bullet}OH + OH^- \qquad (6)$$

$$O^{\bullet -} / {}^{\bullet}OH + (CH_3)_2CH(OH) \rightarrow (CH_3)_2{}^{\bullet}C(OH) + OH^- / H_2O \qquad (7)$$

## 3. Results and Discussion

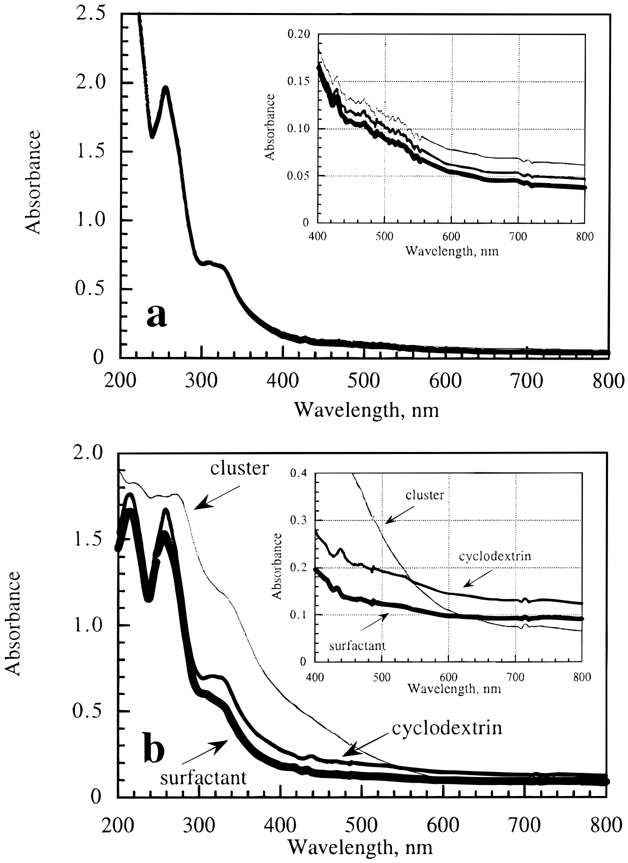

**Figure 2.** Absorption spectra (a) of **2** in $H_2O$/surfactant solution at various water contents and (b) of monomeric **2** in a cetyltrimethylammonium chloride surfactant (bold line), $\gamma$-cyclodextrin (medium line), and colloidal **2** without any additive (thin line).

**Absorption Spectra.** Dissolving fullerene derivatives **1**−**3** in aqueous solution, via suspension in tetrahydrofuran (THF) and subsequent addition of water, leads in general to the irreversible formation of fullerene clusters. This was followed spectroscopically; e.g. the sharp absorption bands of monomeric fullerenes (for example $C_{60}(C_9H_{11}O_2)(COO^-)$ **2**: 215, 258, 310, 416, 524, and 699 nm) transform into broadly absorbing features (around 263, 332, and 435 nm). These spectral differences serve as a sensitive pointer for colloidal $C_{60}$ clusters and resemble those of pristine $C_{60}$ in polar (butanol, propanol, and ethanol) or vesicular media (DODAB, lecithin, and DHP).[19] Addition of a surfactant such as cetyltrimethylammonium chloride or Triton-X 100 to the THF suspension of **1**−**3** prior to the water component prevented aggregation of the fullerene cores and, in turn, resulted in stabilization of fullerene monomers. Figure 2a illustrates, for derivative **2**, that increasing the water content has no impact on the well-resolved absorption features of monomeric $C_{60}(C_9H_{11}O_2)(COO^-)$. Subsequently, evaporation of the THF did not result in any detectable destabilization of the fullerene monomers, e.g. no broadening of the transition bands. This observation can be rationalized in terms of capping the hydrophobic fullerene moiety by the hydrophobic tail of the surfactant in a core(fullerene)−shell(surfactant) structure surrounded, in the case of cetyltrimethylammonium chloride, by a layer of positive charges evolving from the ammonium cation. These capped fullerene monomers were stable in solution and could be kept for days in the dark.

A different approach for the stabilization of fullerene monomers involves accommodation into a water-soluble host.[24,28,29] No spectral evidence for clustering, e.g. preservation of the sharp absorption features at 215, 258, 310, 416, 524, and 699 nm, were found in $\gamma$-cyclodextrin complexes of compounds **1**−**3**. This suggests embedding a single fullerene molecule between the cavity of two $\gamma$-cyclodextrin molecules. Conse-

**TABLE 1: Photophysical Data of Fullerene Clusters 1−3 in Aqueous Media As Derived from Picosecond Measurements**

| compound | $\lambda_{max}$ ($^1C_{60}$)R (nm) | $\lambda_{max}$ ($^3C_{60}$)R (nm) | intersystem crossing (ns) | $\tau_{1/2}$ ($^3C_{60}$)R ($\mu$s) |
|---|---|---|---|---|
| $\{C_{60}C(COO^-)_2\}_n$ (**1**) | 888 | 706 | 1.2 | 0.4[a] |
| $\{C_{60}(C_9H_{11}O_2)(COO^-)\}_n$ (**2**) | 910 | 690 | 1.4 | *b* |
| $\{C_{60}(C_4H_{10}N^+)\}_n$ (**3**) | 920 | 680 | 1.3 | 0.3 |

[a] Taken from ref 18. [b] No observable absorption changes upon nanosecond pulse.

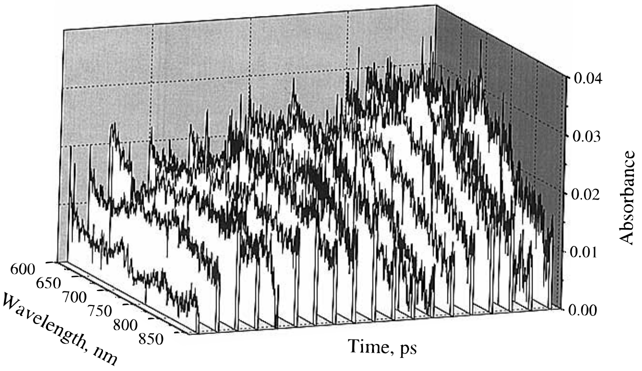

**Figure 3.** Transient absorbance changes observed following picosecond flash photolysis at 355 nm of $[(C_{60})(C_9H_{11}O_2)(COO^-)]_{cluster}$ (**2**) in deaerated aqueous solution. Time scale 50, 100, 150, 200, 250, 300, 400, 500, 600, 800, 1000, 1250, 1500, 2000, 3000, 4000, and 5000 ps.

quently, absorption spectra of compounds **1−3** incorporated into $\gamma$-cyclodextrin are similar to the corresponding surfactant solutions, as shown in Figure 2b for $C_{60}(C_9H_{11}O_2)(COO^-)$ **2**.

**Excited States.** In order to probe the excited singlet and triplet state characteristics of water-soluble $C_{60}$ derivatives **1−3**, time-resolved differential absorption spectra were recorded following picosecond laser excitation. The pump wavelength was 355 nm. Transient absorption spectra of the compounds **1−3** ($[C_{60}(C_9H_{11}O_2)(COO^-)]$ 2.0 × $10^{-5}$ M; monomer concentration) in deoxygenated aqueous solutions reveal the evolution of an absorption around 900 nm (see Table 1) which is completed ca. 100 ps after the pulse. The monitored features closely resemble earlier observations for pristine $C_{60}$ and some functionalized fullerene derivatives in toluene. Thus, the transient absorptions can be unambiguously attributed to the fullerene singlet−singlet ($^*S_1 \rightarrow {}^*S_n$) transition. The decay of the $^*S_1 \rightarrow {}^*S_n$ absorption was found to follow clear first-order kinetics, simultaneously to the formation of a sharp absorption around 700 nm, attributable to the energetically lower lying $^*T_1 \rightarrow {}^*T_n$ transition (Figure 3). The "intersystem crossing" rates of compounds **1−3** were derived from the decay kinetics of the excited singlet states and grow-in kinetics of the excited triplet states. They were typically in the range of 5.0 × $10^8$ $M^{-1}$ $s^{-1}$ (see Figure 4 and Table 1) and are reasonably in line with those found for monomeric solutions of pristine $C_{60}$ or functionalized fullerene derivatives in nonpolar solvents.[30,31,34]

$$[(C_{60})(C_9H_{11}O_2)(COO^-)]_{cluster} \xrightarrow{h\nu} [(^1C_{60})(C_9H_{11}O_2)(COO^-)]_{cluster} \xrightarrow{ISC} [(^3C_{60})(C_9H_{11}O_2)(COO^-)]_{cluster} \xrightarrow{decay} [(C_{60})(C_9H_{11}O_2)(COO^-)]_{cluster} \quad (8)$$

The current observation illustrates that fullerene aggregation does not effect the physicochemical properties related to the generation and lifetime of the excited singlet state which was further substantiated by identical observations for surfactant-capped or $\gamma$-CD-incorporated monomers (**1−3**). This is remarkable, since closely packed thin films of $C_{60}$, as formed upon sublimation, display a fast decay (in the range of 2 ps) of the fullerene excited singlet state.[35] The density dependence of the relaxation process has been interpreted in terms of a fast depopulation of the excited singlet state via singlet−singlet annihilation. Since unambiguous evidence substantiates the cluster concept of compounds **1−3**, the present data suggest much weaker cohesive interaction between the fullerene moieties in aqueous solutions than in thin films. On the subnanosecond time scale, the only noticeable deviation of the processes following photoexcitation between monomeric and colloidal derivatives **1−3** is the position of $\lambda_{max}$ of the corresponding $^*T_1 \rightarrow {}^*T_n$ absorption. The relative positions, however, fall in line with those found for the $\pi$-radical anion absorption (see the pulse radiolysis section) and seem to reflect sensitively the environment of the surrounding medium.

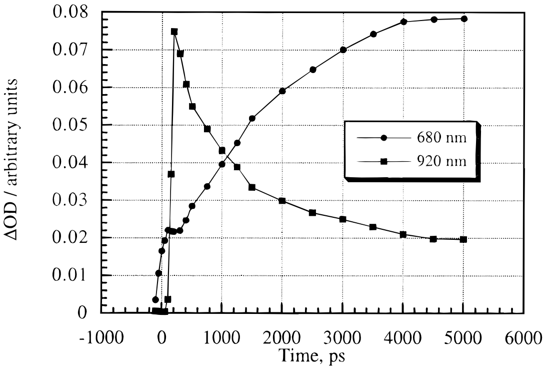

**Figure 4.** Absorption time profile for the decay of $^*S_1 \rightarrow {}^*S_n$ transition (at 920 nm) of $[(^1C_{60})(C_9H_{11}O_2)(COO^-)]_{cluster}$ (**2**) and the growth of $^*T_1 \rightarrow {}^*T_n$ absorption (at 680 nm) of $[(^3C_{60})(C_9H_{11}O_2)(COO^-)]_{cluster}$ (**2**).

**TABLE 2: Photophysical Data of Monomeric Fullerene/$\gamma$-Cyclodextrin Complexes 1−3 in Aqueous Media**

| compound | $\lambda_{max}$ ($^1C_{60}$)R (nm) | $\lambda_{max}$ ($^3C_{60}$)R (nm) | ISC | $\tau_{1/2}$ ($^3C_{60}$)R ($\mu$s) | $k_{quenching}$ (DABCO) ($M^{-1}$ $s^{-1}$) |
|---|---|---|---|---|---|
| $C_{60}/\gamma$-CD[a] | | 750[a] | | | 1.6 × $10^{8}$[a] |
| $C_{60}C(COO^-)_2/\gamma$-CD (**1**) | 890 | 720 | | 59 | 6.9 × $10^6$ |
| $C_{60}(C_9H_{11}O_2)(COO^-)/\gamma$-CD (**2**) | 910 | 710 | | 65 | 6.8 × $10^6$ |
| $C_{60}(C_4H_{10}N^+)/\gamma$-CD (**3**)[b] | 920 | 700 | 1.3 ns | 52 | 2.7 × $10^7$ |

[a] Taken from ref 11. [b] Counter anion is chloride.

**TABLE 3: Photophysical Data of Monomeric Fullerene/Surfactant Complexes 1−3 in Aqueous Media**

| compound | $\lambda_{max}$ ($^3C_{60}$)R (nm) | $\tau_{1/2}$ ($^3C_{60}$)R ($\mu$s) | $k_{quenching}$ (DABCO) ($M^{-1}$ $s^{-1}$) | $\tau_{1/2}$ ($C_{60}{}^{\bullet -}$)R (ms) |
|---|---|---|---|---|
| $[C_{60}]_{surfactant}$[a] | 750[a] | | 7.4 × $10^7$ [a] | 0.44 ms[a] |
| $[C_{60}C(COO^-)_2]_{surfactant}$ (**1**) | 700 | 69 | 4.8 × $10^6$ | 1.1 ms |
| $[C_{60}(C_9H_{11}O_2)(COO^-)]_{surfactant}$ (**2**) | 690 | 63 | 4.9 × $10^6$ | 2.4 ms |
| $[C_{60}(C_4H_{10}N^+)]_{surfactant}$ (**3**)[b] | 690 | 56 | 7.8 × $10^6$ | 1.9 ms |

[a] In Triton X-100, taken from ref 32. [b] Counteranion is chloride.

Although clustering was found to have an insignificant impact on the fate of the excited singlet state, nanosecond studies revealed remarkable changes for the decay of the fullerene excited triplet state. The triplets decayed with $\tau_{1/2}$ = 0.4 and 0.3 $\mu$s for colloidal clusters of **1** and **3**, respectively, to regenerate the ground state. These values are 2 orders of magnitude smaller than those for the corresponding fullerene monomers (see Tables 2 and 3). Since triplet−triplet annihilation determines the decay of the excited triplet state, the current finding can be interpreted in terms of close packing of the fullerene moieties within the

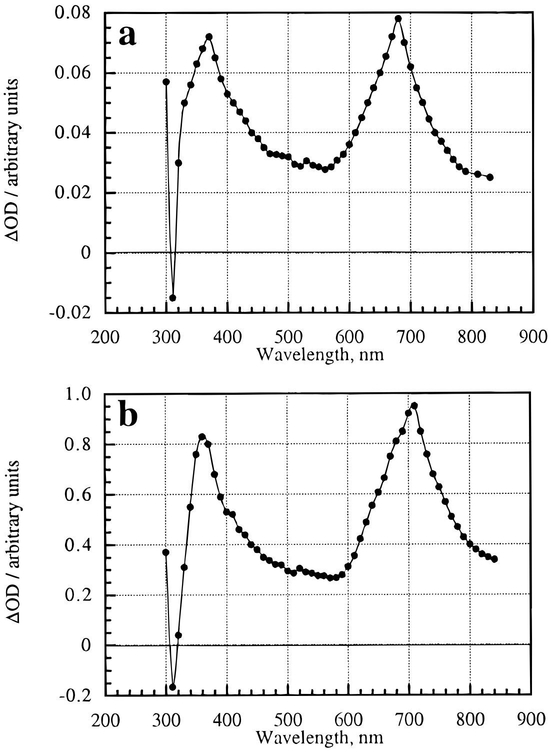

**Figure 5.** Differential absorption spectra obtained upon flash photolysis at 337 nm of (a) 2.0 × $10^{-5}$ M $(C_{60})(C_9H_{11}O_2)(COO^-)$ (**2**)/cetyltrimethylammonium chloride and (b) 2.0 × $10^{-5}$ M $(C_{60})(C_9H_{11}O_2)(COO^-)$ (**2**)/$\gamma$-cyclodextrin in nitrogen-saturated aqueous solution.

apparent clusters, which, in turn, should lead to an acceleration of the decay process. Furthermore, the lack of any detectable $^*T_1 \rightarrow {}^*T_n$ absorption for **2** corroborates this assumption.

Shielding individual fullerene cores from each other, as can be assumed in surfactant-capped or $\gamma$-CD-incorporated monomeric derivatives **1**−**3**, is expected to discriminate cluster-induced quenching. Indeed, nanosecond-resolved photolysis of monomeric derivatives **1**−**3**, either capped by surfactants or $\gamma$-CD-incorporated, revealed the immediate formation of a long-lived $^*T_1 \rightarrow {}^*T_n$ absorption. Nanosecond photolysis of 2.0 × $10^{-5}$ M $[(C_{60})(C_9H_{11}O_2)(COO^-)]_{surfactant}$ **2** in deoxygenated aqueous solutions produced transient absorption changes which are shown in Figure 5 a,b. An immediate bleaching of the ground state absorbance around 310 nm due to the conversion of the ground state to the excited triplet state was monitored, with the concomitant generation of some new absorption around 380 and 700 nm. The differential absorption spectra are reminiscent of those reported for the excited triplet states of various monofunctionalized fullerene derivatives in aprotic media.[12,14,15] Kinetic analysis of both bleaching and formation time−absorption profiles revealed a recovery of the transient absorption to the original base line in an exponential manner. This indicates no noticeable chemical reaction of the photoexcited fullerenes with the surfactant or $\gamma$-CD host. The excited triplet states decayed with half-lives typically in the range of 52−69 $\mu$s (Tables 2 and 3). These values are reasonably in line with previously reported values for pristine $C_{60}$ systems.[21,32]

It should be noted that in surfactant-capped $C_{60}(C_4H_{10}N^+)/I^-$ **3** solutions the lifetime of the excited triplet state was (i) significantly decreased relative to those found for derivatives **1** and **2** and (ii) dependent on the $[C_{60}(C_4H_{10}N^+)/I^-]_{surfactant}$ concentration (even at concentrations lower than 2.0 × $10^{-5}$ M). Iodide and $(C_6H_{14}N^+)/I^-$ are efficient quenchers of $[^3C_{60}]_{surfactant}$ and $^3C_{60}/\gamma$-CD with a calculated rate constant of 5 × $10^8$ $M^{-1}$ $s^{-1}$ (for $(C_6H_{14}N^+)/I^-$). In contrast, addition of up to 1 × $10^{-2}$ M $(C_6H_{14}N^+)/Cl^-$ did not result in any noticeable quenching of $[^3C_{60}]_{surfactant}$ which suggests that the reduced lifetime of the excited triplet state of **3** is due to iodide-related quenching.

**Reductive Quenching of Monomeric Fullerene Derivatives.** Diazabicyclooctane (DABCO) has been shown to be an efficient one-electron quencher of excited triplet states of fullerenes, yielding $C_{60}^{\bullet-}$ and $(DABCO)^{\bullet+}$ in high yields.[15,32] However, the short lifetime of excited triplet fullerene clusters **1**−**3** precludes meaningful quenching studies of this short-lived transient. On the other hand, surfactant solutions and inclusion complexes of pristine $C_{60}$ with $\gamma$-cyclodextrin have been shown to provide environments that (i) exclude fullerene aggregation, (ii) support rapid reductive quenching, and (iii) suggest stabilization of a long-lived charge-separated radical pair.

Addition of various concentrations of DABCO in the range of (1−5) × $10^{-3}$ M to a deoxygenated solution of capped fullerene derivatives **2** (2.0 × $10^{-5}$ M fullerene and $10^{-3}$ M cetyltrimethylammonium chloride) resulted in an accelerated decay of the excited triplet state absorption around 380 and 700 nm and an accelerated recovery of the bleaching at 310 nm. Following the decay of the $^*T_1 \rightarrow {}^*T_n$ absorption at 690 nm allowed the determination of the rate constant for the possible quenching reaction. The observed rate ($k_{obs} = \ln 2/\tau_{1/2}$) was linearly dependent on the DABCO concentration, indicating that the underlying process can be attributed to a quenching of $[(^3C_{60})(C_9H_{11}O_2)(COO^-)]_{surfactant}$. From the slope of the plot of $k_{obs}$ versus DABCO concentration, a value of 4.9 × $10^6$ $M^{-1}$ $s^{-1}$ for $k_{quenching}$ was determined. Essentially similar results were obtained upon addition of DABCO to capped fullerene derivatives **1** and **3**.

In the presence of DABCO, the $^*T_1 \rightarrow {}^*T_n$ absorption did not recover to the base line. Furthermore, differential absorption changes in the near-IR region indicated that the decay of the $[(^3C_{60})(C_9H_{11}O_2)(COO^-)]_{surfactant}$ occurs synchronously with a grow-in of the characteristic $[(C_{60}^{\bullet-})(C_9H_{11}O_2)(COO^-)]_{surfactant}$ transition band with $\lambda_{max}$ at 1010 nm (not shown). This suggests that formation of the fullerene $\pi$-radical anion evolves from electron transfer to the photoexcited fullerene moiety from DABCO. The high dielectric medium and the nature of the core(fullerene)−shell(surfactant) structure promote stabilization of a long-lived charge-separated state with $\tau_{1/2}$ between 1.1 and 2.4 ms. Similar observations were made with $\gamma$-CD-incorporated complexes **1**−**3**. The respective rates are listed in Table 2. The remarkable discrepancies relative to capped fullerene derivatives **1**−**3** are (i) a diminished efficiency of the quenching process and (ii) a reduced lifetime of the charge-separated states (see Tables 2 and 3).

The rate constants for the positively charged fullerene derivative **3**, either surfactant-capped or $\gamma$-CD-incorporated, display a 2-fold enhancement over compounds **1** and **2** which bear one or two negatively charged carboxyl groups, respectively. The faster quenching indicates an anodic-shifted reduction potential of **3** relative to **1** and **2**. This observation can be rationalized in terms of the higher electron-withdrawing effects induced by the functional groups of derivatives **1** and **2** as compared to the quartery ammonium cation in $C_{60}(C_4H_{10}N^+)$ **3**.

**Radiolytic Reduction.** Pulse radiolysis is an important source for fast kinetic spectroscopic studies and has been complementary employed for the generation of $\pi$-radical anions of pristine fullerenes and functionalized fullerene derivatives.[9−11,33] As a consequence of the moderate redox potential of pristine $C_{60}$, e.g. $E_{1/2}$ $[C_{60}/C_{60}^{\bullet-}] = -0.4$ V versus SCE, radical-induced reduction by hydrated electrons or $(CH_3)_2{}^{\bullet}C(OH)$ radicals take place rapidly with rate constants of 1.8 × $10^{10}$ and 8.5 × $10^8$

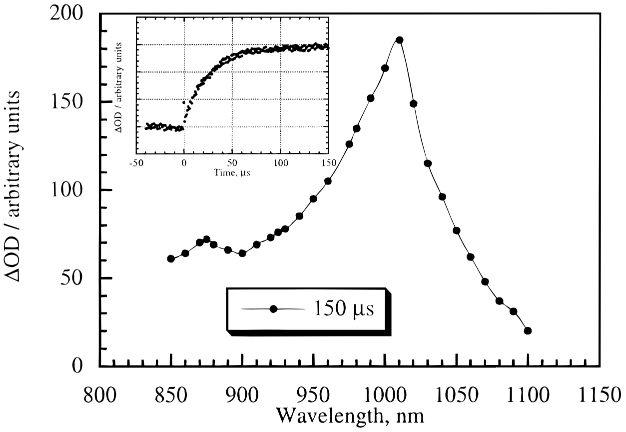

**Figure 6.** Transient absorption spectrum (near-IR) of $[(C_{60}^{\bullet -})(C_9H_{11}O_2)(COO^-)]_{surfactant}$ obtained upon pulse radiolysis of $2.0 \times 10^{-5}$ M $[C_{60}(C_9H_{11}O_2)(COO^-)]_{surfactant}$ ($10^{-3}$ M cetyltrimethylammonium chloride) in nitrogen-saturated aqueous solution (10 vol % 2-propanol). Inset : Time-absorption profile at 1015 nm.

$M^{-1}$ $s^{-1}$, respectively.[10] Surprisingly, pulse radiolysis experiments failed to substantiate any reduction of compounds **1** and **2** in aqueous solution.[18] The decay of the hydrated electron at 720 nm was virtually unaffected irregardless of the applied fullerene concentration [monomer concentration $(0.5-10) \times 10^{-5}$ M]. The lack of any detectable absorption changes in the near-IR, which are attributable to the fullerene π-radical anion ($C_{60}^{\bullet -}$), further corroborates this observation and was rationalized in terms of clustering.

A promising approach to resolve the difficulties that are associated with this aggregation phenomenon focuses on capping fullerenes with surfactants or incorporating them into host molecules that support stabilization of monomeric fullerene derivatives. Surfactants, such as Triton X-100 or BRIJ 35, and supramolecular γ-cyclodextrin have been shown to be suitable for this purpose.[19] Complementary studies of complexes with pristine $C_{60}$, e.g. $[C_{60}]_{surfactant}$ and $C_{60}$/γ-CD, indicated rapid reduction of the fullerene moiety.

Differential absorption changes at 720 nm (absorption maximum of the hydrated electron) and throughout the near-IR (Figure 6), recorded upon pulse radiolysis of surfactant-capped $[C_{60}(C_9H_{11}O_2)(COO^-)]_{surfactant}$ ($2.0 \times 10^{-5}$ M fullerene and $10^{-3}$ M cetyltrimethylammonium chloride) in deoxygenated aqueous/2-propanol solution (9:1 v/v) confirm that this fullerene monomer is susceptible for reduction. Variation of the $[C_{60}(C_9H_{11}O_2)(COO^-)]_{surfactant}$ **2** concentration ($(0.2-4.0) \times 10^{-5}$ M) impacted the decay of the hydrated electron absorption at 720 nm in a linear manner. The underlying rate was found to be dependent on the fullerene concentration and, furthermore, in excellent agreement with the rate of formation of the fullerene π-radical anion (1010 nm). This suggests that the observed reaction can be unambiguously ascribed to reduction of the fullerene complex by hydrated electrons.

$$[C_{60}(C_9H_{11}O_2)(COO^-)]_{surfactant} + e_{aq}^- \rightarrow [(C_{60}^{\bullet -})(C_9H_{11}O_2)(COO^-)]_{surfactant} \quad (9)$$

The rate constant is $2.3 \times 10^{10}$ $M^{-1}$ $s^{-1}$ which is only slightly faster than the one found for the inclusion complex of $C_{60}(C_9H_{11}O_2)(COO^-)$ **2** in γ-CD ($9.2 \times 10^9$ $M^{-1}$ $s^{-1}$).[16]

Radiolysis of oxygen-free aqueous/2-propanol solutions results in the generation of strongly reducing $(CH_3)_2{}^\bullet C(OH)$ radicals (see eqs 1−7). This α-hydroxyalkyl radical is expected to transfer an electron to the fullerene core with rate constants of ∼$8 \times 10^8$ $M^{-1}$ $s^{-1}$, as observed for pristine $C_{60}$.[3] Indeed, absorption time profiles throughout the near-IR region display, besides the fast electron related reduction, a slower exponential formation component. This evolves from electron transfer to yield $[(C_{60}^{\bullet -})(C_9H_{11}O_2)(COO^-)]_{surfactant}$ on a time scale of a few hundred microseconds (see for illustration inset to Figure 6). The resulting differential absorption spectrum (∼150 μs after the pulse) closely resembles that assigned upon electron-induced formation of the fullerene π-radical anion, e.g. ∼5 μs after the pulse.

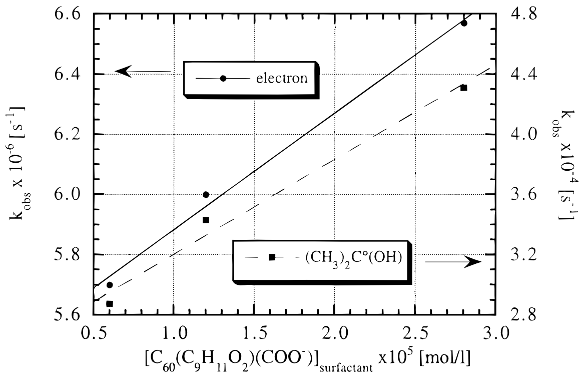

**Figure 7.** Plot of $k_{obs}$ versus $[(C_{60})(C_9H_{11}O_2)(COO^-)]_{surfactant}$ at 720 nm (hydrated electron) and 1015 nm ($(CH_3)_2{}^\bullet C(OH)$ radical) for the reduction of monomeric fullerene derivative **2** in deoxygenated aqueous solution (10 vol % 2-propanol).

**TABLE 4: Rate Constant ($k_{reduction}$) and Absorption Maxima ($\lambda_{max}$) for the Radiolytic Reduction of Monomeric Fullerene/Surfactant Complexes 1−3 in Aqueous Media**

| compound | $k_{reduction}$ ($e_{aq}^-$) ($M^{-1}$ $s^{-1}$) | $k_{reduction}$ ($(CH_3)_2{}^\bullet C(OH)$) ($M^{-1}$ $s^{-1}$) | $\lambda_{max}$ ($C_{60}^{\bullet -}$)R (nm) |
|---|---|---|---|
| $[C_{60}C(COO^-)_2]_{surfactant}$ (**1**) | $1.7 \times 10^{10}$ | $5.4 \times 10^8$ | 1015 |
| $[C_{60}(C_9H_{11}O_2)(COO^-)]_{surfactant}$ (**2**) | $2.3 \times 10^{10}$ | $6.1 \times 10^8$ | 1010 |
| $[C_{60}(C_4H_{10}N^+)]_{surfactant}$ (**3**) | $3.5 \times 10^{10}$ | $7.7 \times 10^8$ | 1015 |

$$[C_{60}(C_9H_{11}O_2)(COO^-)]_{surfactant} + (CH_3)_2{}^\bullet C(OH) \rightarrow [(C_{60}^{\bullet -})(C_9H_{11}O_2)(COO^-)]_{surfactant} + (CH_3)_2CO + H^+ \quad (10)$$

The associated kinetics are linearly dependent on the fullerene concentration (Figure 7) with a rate constant of $6.1 \times 10^8$ $M^{-1}$ $s^{-1}$. The lower rate constant relative to pristine $C_{60}$ can be correlated to the cathodic shift of the reduction potential that is associated with functionalization of the fullerene moiety. Saturation of the fullerene solution with $N_2O$ instead of $N_2$ leads to a conversion of $e_{aq}^-$ to hydroxyl radicals and, subsequently, to $(CH_3)_2{}^\bullet C(OH)$ radicals (see eqs 5−7). As a consequence no evidence for any electron-related reduction was observed in the corresponding experiments.

Radiolytic reduction of surfactant-capped derivatives **1** and **3** in aqueous media resulted in similar findings (Table 4). Electron transfer from $e_{aq}^-$ and $(CH_3)_2{}^\bullet C(OH)$ radicals yielded $[(C_{60}^{\bullet -})C(COO^-)_2]_{surfactant}$ **1** and $[(C_{60}^{\bullet -})(C_4H_{10}N^+)]_{surfactant}$ **3**, with characteristic transition bands at 1015 nm. The underlying rate constants are similar to the earlier values reported for monomeric γ-CD complexes of **1** and **3**.[16] The presence of a quartery ammonium group exerts electron-attracting forces on the fullerene moiety and, thus, accelerates the reduction of $[C_{60}(C_4H_{10}N^+)]_{surfactant}$ **3** by hydrated electrons and $(CH_3)_2{}^\bullet C(OH)$ radicals relative to the negatively charged systems **1** and **2**.

It is interesting to note that the $\lambda_{max}$ of the π-radical anions **1**−**3** is very sensitive to the environmental parameters of the accommodating assembly. In surfactant media, the maxima ($[(C_{60}^{\bullet -})(C_4H_{10}N^+)]_{surfactant}$ 1015 nm) were generally blue-shifted relative to the analogous $\gamma$-CD complexes ($[(C_{60}^{\bullet -})(C_4H_{10}N^+)]/\gamma$-CD 1030 nm), similar to the blue-shift observed for the promptly reduced cluster ($[(C_{60}^{\bullet -})(C_4H_{10}N^+)]_n$ 1010 nm). In nonaqueous media, e.g., toluene/2-propanol/acetone (8:1:1 v/v), radiolytic reduction of *N*-methylfulleropyrrolidine ($C_{60}(C_3H_7N)$) results in the formation of a characteristic $\pi$-radical anion band positioned at 1025 nm. This leads to the hypothesis that inside the $\gamma$-CD cavity the fullerene moiety is efficiently shielded from the aqueous phase, comparable to the environmental parameters of *N*-methylfulleropyrrolidine in toluene. In surfactant-based core(fullerene)−shell(surfactant) structures the dynamic exchange of surfactant molecules allows contact with the surrounding aqueous phase and, thus, alters the environment of the fullerene core. Further support for this assumption emerges from studies on the radiolytic formation of equatorial $(C_{60}^{\bullet -})$-$[C(COOEt)_2]_2$ [15] in nonpolar toluene and its hydrolyzed analogue, e.g. equatorial $(C_{60}^{\bullet -})[C(COO^-)_2]_2$,[16] in aqueous media, which shows a bathochromic shift from 1065 to 1050 nm, respectively.

Finally, it should be emphasized that the good agreement of the rate constants for the reduction of fullerene derivatives **1**−**3** embedded in cetyltrimethylammonium chloride, by hydrated electrons and also $(CH_3)_2{}^{\bullet}C(OH)$ radicals, with those reported earlier for the corresponding $\gamma$-cyclodextrin complexes substantiates the stabilization of fullerene monomers in surfactant solutions. Aggregation, as observed for homogeneous aqueous media, would affect the true fullerene concentration and the derived rate constants.

## 4. Conclusion

A promising approach overcoming the water insolubiltiy of pristine fullerenes is the amphiphilic functionalization of pristine $C_{60}$ via covalent attachment of hydrophilic addends. Functionalization of $C_{60}$ with hydrophilic ligands successfully promotes the water solubility of the fullerene core. The data presented here on the functionalization of $C_{60}$ show that one hydrophilic addend is not sufficient to prevent the strong hydrophobic three-dimensional interactions among the fullerene moieties and the resulting tendency to form aggregates. Capping the surface of water-soluble fullerene derivatives with surfactants, however, was found to exclude formation of fullerene clusters.

Flash photolytic techniques were employed to generated excited states of fullerene monomers and fullerene clusters **1**−**3**. Differential absorption revealed spectral characteristics of the respective ${}^*S_1 \rightarrow {}^*S_n$ absorptions which were found to be independent of the aggregation state, e.g. monomer versus cluster. The intersystem crossing rates to the excited triplet state for fullerene clusters **1**−**3** closely resembled those of various monofunctionalized fullerene derivatives in nonpolar solutions. Although the cluster packing did not impact the fullerene's intersystem crossing, triplet−triplet annihilation in these systems apparently leads to an acceleration of the decay process with values 2 orders of magnitude faster ($\tau_{1/2} = 0.4$ and 0.3 $\mu$s for colloidal clusters of **1** and **3**) than those for the corresponding fullerene monomers. Capping derivatives **1**−**3** with surfactants or incorporation into the cavity of $\gamma$-CD effectively shields individual fullerene cores from each other and prevents cluster-induced quenching of the excited triplet state. In line with this hypothesis monomeric derivatives **1**−**3** revealed the formation of long-lived ${}^*T_1 \rightarrow {}^*T_n$ absorptions.

The rate constants for the reduction of $[C_{60}(C_4H_{10}N^+)]_{\text{surfactant}}$, and as earlier reported for $C_{60}(C_4H_{10}N^+)]/\gamma$-CD, by hydrated electrons show an enhancement over pristine $C_{60}$ and negatively charged analogues of **1** and **2**, e.g. surface-capped or $\gamma$-CD-incorporated. This can be rationalized in terms of elimination of the charge-repelling forces, which decelerates a reaction between hydrated electrons and the negatively charged fullerenes and facilitates reduction of the positively charged fullerenes.

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