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LETTERS

Radiolytic Reduction of a Water-Soluble Fullerene Cluster

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In the present Letter we extend our previous studies on negatively charged fullerene clusters $\{C_{60}C(COO^-)_2\}_n$, **2**, and $\{C_{60}(C_9H_{11}O_2)(COO^-)\}_n$, **3**, to a functionalized derivative which carries a positive charge $\{C_{60}(C_4H_{10}N^+)\}_n$, **1b**. It will be demonstrated that covalent introduction of a quartery ammonium group at the fullerene moiety, via *N*-methylation of **1a** (*N*-methylfulleropyrrolidine $C_{60}(C_3H_7N)$, not only enhances the water-solubility but the positive charge also enhances the rate of reduction of the fullerene core in a cluster to yield $\{(C_{60}^{\bullet -})(C_4H_{10}N^+)\}_n$.

Suitably functionalized fullerene derivatives have found a number of important applications in fields ranging from optical limiting[1] to various topics in biological chemistry, such as enzyme inhibition, antiviral activity, DNA cleavage, and photodynamic therapy.[2] Synthesis of water-soluble adducts of this spherical carbon allotrope became a particularly challenging topic in connection with potential biological applications.[3] Two of them, namely $C_{60}C(COO^-)_2$, **2**, and $C_{60}(C_9H_{11}O_2)(COO^-)$, **3** (see Figure 1), have already been subject of radiolytic studies on their reduction by hydrated electrons and other reducing radicals. Surprisingly, **2** and **3** seemed to exhibit no noticeable reaction of the fullerene cores with any reductive species.[4] These observations were rationalized in terms of clustering in which the hydrophobic fullerene moiety is centered in a core-shell structure surrounded by a layer of negative charges from the carboxyl groups. The concept of reduction-inert clusters was substantiated by complementary photolytic and electrochemical studies.[4a,5]

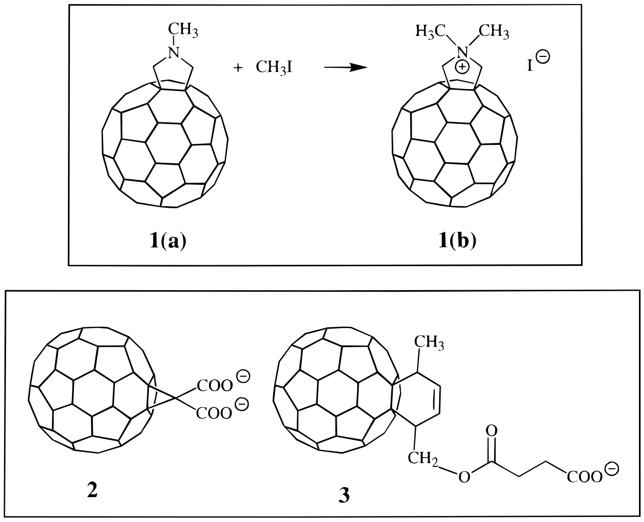

Figure 1. Reaction scheme for the synthesis of **1b** and compounds referred to in this study.

It is conceivable that elimination of the charge-repelling forces, which prevented a reaction between e_{aq}^- and the negatively charged fullerenes **2** and **3**, should facilitate reduction of the positively charged fullerene $C_{60}(C_4H_{10}N^+)$ to yield $(C_{60}^{\bullet -})(C_4H_{10}N^+)$.

In another type of study it has been found that, upon diminishing the fullerene's hydrophobic surface via covalent func-

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TABLE 1: Rate Constant for the Reduction of $\{C_{60}(C_4H_{10}N^+)\}_n$ Cluster and $C_{60}(C_4H_{10}N^+)$ Monomers by the Hydrated Electron ($e_{aq}-$) and $(CH_3)_2{}^{\bullet}C(OH)$ Radicals in Aqueous Media

compound	$e_{aq}-$; k (10^{10} M^{-1} s^{-1})	$(CH_3)_2{}^{\bullet}C(OH)$; k (10^8 M^{-1} s^{-1})
$\{C_{60}(C_4H_{10}N^+)\}_n$	0.36	9.0[a]
$C_{60}(C_4H_{10}N^+)/\gamma$-CD	2.8	5.1
$C_{60}(C_4H_{10}N^+)$/surfactant	3.5	7.7

[a] Only one concentration.

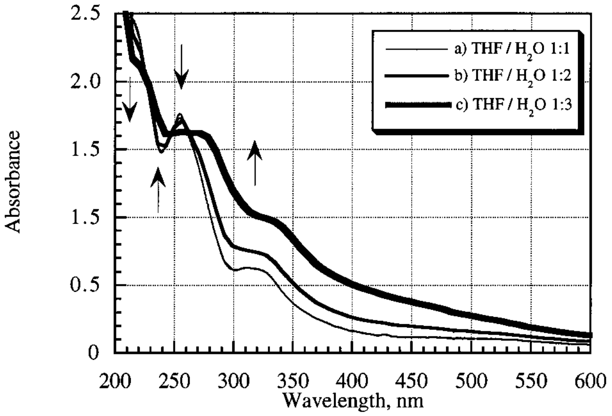

Figure 2. Ground state absorption spectra (UV−vis) of 2.8 × 10^{-5} M $C_{60}(C_4H_{10}N^+)$ **1b** in (a) THF/H_2O (1:1) (thin line); (b) THF/H_2O (1:2) (medium line); (c) THF/H_2O (1:3) (thick line).

tionalization, the electron acceptor properties are substantially impacted.[6] For example, the reduction of the ground ($C_{60}/C_{60}{}^{\bullet-}$) and excited states ($^*C_{60}/C_{60}{}^{\bullet-}$) are shifted to more cathodic potentials with increasing number of functionalizing addends.[6]

A convenient way to dissolve the quatery ammonium salt $C_{60}(C_4H_{10}N^+)/I^-$, **1b**, in aqueous solution involves suspension in tetrahydrofuran (THF), addition of water, and subsequent evaporation of the organic component. This procedure allows one to follow the cluster formation spectroscopically as illustrated in Figure 2. The sharp absorption features of monomeric **1b** at 216, 254, 313, 426, 519, and 688 nm diminish with increasing water content in the solvent mixture. Instead, the absorption spectra seem to transform into broad bands around 263, 332, and 435 nm (arrows indicating this transformation), in close resemblance to Langmuir−Blodgett films of C_{60} and functionalized fullerene derivatives on a quartz substrate.[7] The spectral changes of the UV−vis bands are regarded as an indicator for the formation of colloidal $\{C_{60}(C_4H_{10}N^+)\}_n$ clusters. Cluster formation could be prevented if a surfactant, e.g. Triton-X 100 or cetyltrimethylammonium chloride, was added to the solvent THF prior to the suspension of **1b**. Once the cluster has been formed, it was, however, impossible to disintegrate it again by addition of the surfactant. The failure to redissolve colloidal fullerene clusters by subsequent addition of Triton-X 100 or cetyltrimethylammonium chloride indicates strong and irreversible aggregation forces.

Reduction of $\{C_{60}(C_4H_{10}N^+)\}_n$ clusters were studied in aqueous solution containing 10 vol % 2-propanol, making use of the known characteristics of the $C_{60}{}^{\bullet-}$ moiety (particularly an absorption band in the near-IR).[8] Radiolysis of this system leads to the generation of strongly reducing species, namely, hydrated electrons and $(CH_3)_2{}^{\bullet}C(OH)$ radicals. Pulse radiolysis of an N_2-purged solution of 2 × 10^{-5} M $C_{60}(C_4H_{10}N^+)$ (monomer concentration) yielded a differential spectrum, the near-IR part of which is shown in Figure 3a. These spectral changes indicate one-electron reduction of the fullerene cluster to its π-radical anion, by comparison with results on pristine C_{60},[8] and from the close resemblance of the observed absorption maximum at 1010 nm with that found upon radiolysis of *N*-methylfulleropyrrolidine ($C_{60}(C_3H_7N)$) **1a** in aprotic media.[9]

$$\{C_{60}(C_4H_{10}N^+)\}_n + e_{aq}- \rightarrow \{(C_{60}{}^{\bullet-})(C_4H_{10}N^+)\}_n \quad (1)$$

It is interesting to note that λ_{max} of the IR absorption band (1010 nm) is considerably blue-shifted relative to the 1080 nm position for pristine $C_{60}{\bullet}^-$. Such an effect reflects the perturbation of the fullerene π-system by the introduction of the functional group.[6]

Accelerated formation of the fullerene π-radical anion (monitored at 1010 nm) and decay of the hydrated electron absorption (at 720 nm) were found upon increasing the fullerene concentration ((2.0−0.3) × 10^{-5} M, monomer concentration). The respective first-order rate constant *versus* concentration dependencies (Figure 4) are linear and in good agreement with each other, allowing evaluation of a bimolecular rate constant of 3.6 × 10^9 M^{-1} s^{-1} for the electron-induced reduction of the $\{C_{60}(C_4H_{10}N^+)\}_n$ cluster. This rate constant was determined, incidentally, on the basis of the monomer concentration, i.e. without accounting for the true cluster size. Thus, the absolute rate constant for the reduction of the cluster would still require correction for the agglomeration number (see further below). In any case, there is no question about an efficient reduction of the positively charged cluster by hydrated electrons, i.e. the expected different behavior as compared to the negatively charged cluster.

The time-absorption profile recorded at 1010 nm in the presence of 10 vol % 2-propanol, as depicted in the insert of Figure 3a, indicates that the rapid reduction of the fullerene by hydrated electrons is followed by yet a second, slower process. The latter is attributed to a reaction of the $\{C_{60}(C_4H_{10}N^+)\}_n$ cluster with $(CH_3)_2{}^{\bullet}C(OH)$ radicals. These radicals, which result from the reaction of $^{\bullet}OH$ and $^{\bullet}H$ radicals with $(CH_3)_2CH(OH)$, are powerful reductants and have been shown to reduce, for example, pristine C_{60} rapidly.[8b,d] Differential absorption changes recorded about 200 μs after the pulse, e.g. at a time where the $(CH_3)_2{}^{\bullet}C(OH)$-induced reaction is completed, closely resemble the one shown in Figure 3a. This substantiates formation of $\{(C_{60}{}^{\bullet-})(C_4H_{10}N^+)\}_n$ via electron transfer from $(CH_3)_2{}^{\bullet}C(OH)$. The bimolecular rate constant for this process is estimated to 9.0 × 10^8 M^{-1} s^{-1} (only one concentration).

Fullerenes and functionalized fullerene derivatives escape clustering in aqueous solution upon embedding the monomer fullerene molecules into the cavity of γ-cyclodextrin.[4a,8d,10] Rate constants for these monomer γ-cyclodextrin complexes have been determined for the reactions of hydrated electrons with pristine C_{60}/γ-CD (1.8 × 10^{10} M^{-1} s^{-1}),[8d] $C_{60}C(COO^-)_2/\gamma$-CD, **2**, (9.8 × 10^9 M^{-1} s^{-1}),[4a] and $C_{60}(C_9H_{11}O_2)(COO^-)/\gamma$-CD, **3**, (9.2 × 10^9 M^{-1} s^{-1}).[4b] Corresponding studies with the present positively charged fullerene gave the following results: (i) ground state absorption of aqueous solutions of up to 3.0 × 10^{-4} M $C_{60}(C_4H_{10}N^+)/\gamma$-CD, **1b**, revealed no spectral evidence for agglomeration of the fullerene cores; (ii) pulse radiolysis of 1.5 × 10^{-5} M $C_{60}(C_4H_{10}N^+)/\gamma$-CD, **1b**, in deoxygenated aqueous solution resulted in a differential spectrum with a sharp absorption around 1030 nm (Figure 3b). By similarity to the observations with $\{C_{60}(C_4H_{10}N^+)\}_n$, the observed spectra indicate that the fullerene core is reduced to its π-radical anion, $(C_{60}{}^{\bullet-})(C_4H_{10}N^+)/\gamma$-CD in this complex.

$$C_{60}(C_4H_{10}N^+)/\gamma\text{-CD} + e_{aq}{}^-/(CH_3)_2{}^{\bullet}C(OH) \rightarrow (C_{60}{}^{\bullet-})(C_4H_{10}N^+)/\gamma\text{-CD} + (CH_3)_2CO + H^+ \quad (2)$$

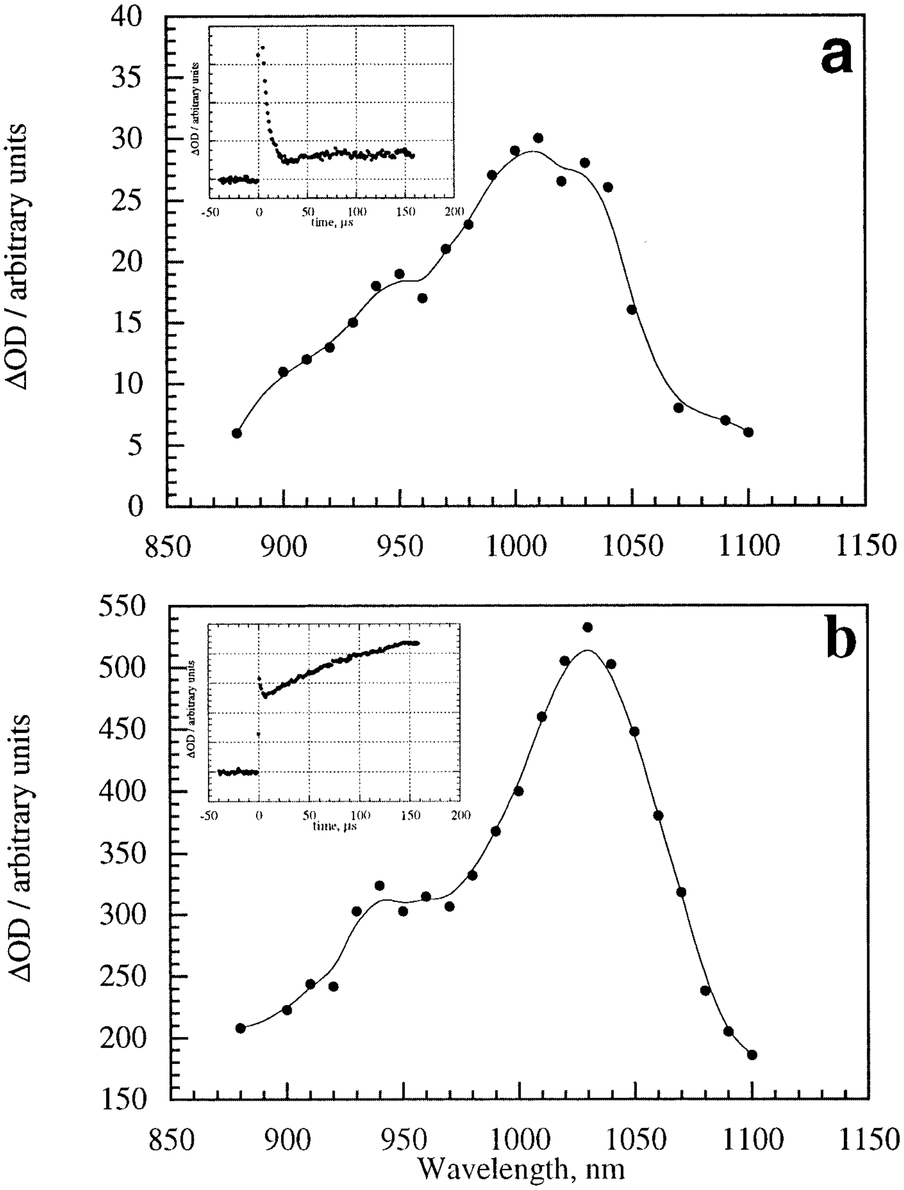

Figure 3. Transient near-IR spectrum of (a) $\{(C_{60}{}^{\bullet-})(C_4H_{10}N+)\}_n$ π-radical anion obtained ca. 25 μs after pulse irradiation of 2×10^{-5} M C_{60}-$(C_4H_{10}N^+)$ **1b** (monomer concentration) and (b) $(C_{60}{}^{\bullet-})(C_4H_{10}N^+)/\gamma$-CD π-radical anion obtained ca. 15 μs after pulse irradiation of 2×10^{-5} M $C_{60}(C_4H_{10}N^+)/\gamma$-CD **1b** in a N_2-purged aqueous solution containing 10 vol % 2-propanol.

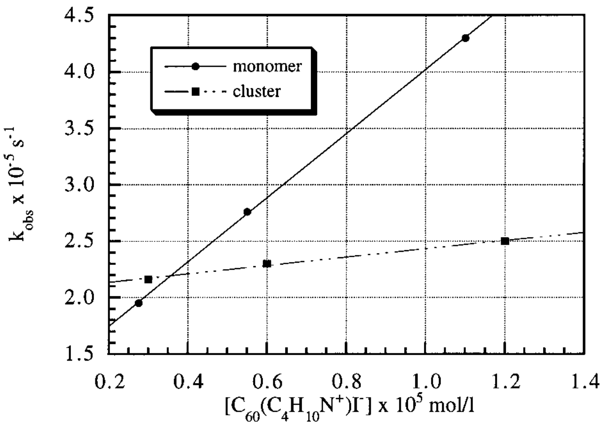

Figure 4. Plot of k_{obs} vs $[C_{60}(C_4H_{10}N^+)]$ and $[C_{60}(C_4H_{10}N^+)/\gamma$-CD$]$ for the reaction of the hydrated electron with $\{C_{60}(C_4H_{10}N^+)\}_n$ clusters (■) and $C_{60}(C_4H_{10}N^+)/\gamma$-CD monomers (●), monitored at 720 nm.

Compared to the reduced fullerene cluster (Figure 3a), there are, however, significant differences. The spectral features of the γ-CD-incorporated monomer are much sharper, which is taken as conclusive support for the cluster concept. This assumption is corroborated by higher yields of the reduced monomer, recorded under similar experimental conditions (Figure 3b), compared to the reduced cluster (Figure 3a).

The corresponding rate constants for the reduction of C_{60}-$(C_4H_{10}N^+)/\gamma$-CD by hydrated electrons and $(CH_3)_2{}^{\bullet}C(OH)$ radicals amount to 2.8×10^{10} M^{-1} s^{-1} (see Figure 4) and 5.1×10^8 M^{-1} s^{-1}, respectively. In the case of the hydrated electron, the rate enhancement over pristine C_{60} and negatively charged complexes of **2** and **3** are plausibly rationalized in terms of charge attracting versus repelling forces relative to pristine C_{60}. Within the γ-CD complexes the respective functional group is considered to stick out into the aqueous phase at one end of the complex. The positively charged quartery ammonium group thus provides an attractive entrance route for the reducing radical. The negatively charged carboxyl group, in **2** and **3**, on the other hand, is likely to completely obstruct one of the two access channels for the electron into the γ-CD moiety.

Very similar rate constants, e.g. 3.5×10^{10} M^{-1} s^{-1} (hydrated electron) and 7.7×10^8 M^{-1} s^{-1} ($(CH_3)_2{}^{\bullet}C(OH)$ radicals), were also derived from reduction experiments with $C_{60}(C_4H_{10}N^+)$

monomers that were stabilized in a surfactant environment (cetyltrimethylammonium chloride) instead of γ-CD.

The ratio of the two rate constants for the electron-induced reduction of the fullerene cluster and the γ-CD-encapsulated monomer is about 1:8. This may be taken as a crude measure for the agglomeration number. Studies on this, using dynamic light scattering and gel exclusion chromatography, are currently under way to determine it with higher accuracy.

In conclusion, attachment of quartery ammonium groups facilitates rapid reduction of fullerene clusters by hydrated electrons and $(CH_3)_2{}^{\bullet}C(OH)$ radicals as compared to the negatively charged systems **2** and **3**. The electron-attracting forces exerted by the positive charge not only accelerate the reduction of $C_{60}(C_4H_{10}N^+)/\gamma$-CD **1b**, relative to the corresponding complexes of **2** and **3**, but also display an enhancement compared to γ-CD-encapsulated pristine C_{60}.

Experimental Section

Synthesis of *N*-methylfulleropyrrolidine ($C_{60}(C_3H_7N)$ **1a**) was carried out following a method described already.[11]

Synthesis of $C_{60}(C_4H_{10}N^+)$ 1b. 50 mg of purified **1a** were dissolved in 30 mL of toluene, and subsequently 20 mL of CH_3I were added dropwise to the solution. The homogeneous mixture was stirred in the dark at room temperature for 2 days. The brown precipitate that quantitatively yielded the toluene-insoluble product $C_{60}(C_4H_{10}N^+)$, **1b**, was filtered off. The purity of **1b** was confirmed by thin layer chromatography with toluene on silica indicating no residue of **1a**.

Selected spectroscopic data for compound **1b** in the UV−vis are (λ_{max}/nm, THF) 215, 255, 310, 324, 427, 514, 686; FAB-MS, m/e 792.

The procedure for the preparation of $C_{60}(C_4H_{10}N^+)/\gamma$-cyclodextrin ($C_{60}(C_4H_{10}N^+)/\gamma$-CD) complex is described in detail in reference 8e.

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.[12b] 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).[12] The radical concentration generated per pulse amounts to $(1-3) \times 10^{-6}$ M for all the systems investigated in this study.

Absorption spectra were recorded with a Milton Roy Spectronic 3000 Array spectrophotometer.

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