

Excited states and electron transfer reactions of $C_{60}(OH)_{18}$ in aqueous solution

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Dynamic light scattering of fullereneol solutions [$C_{60}(OH)_{18}$] reveals evidence for the formation of fullerene aggregates at high solute concentration (up to 3.85×10^{-2} mol dm⁻³). This hydrophilic fullerene derivative emits very weak fluorescence regardless of its concentration. Photolysis (35 ps; $\lambda_{ex} = 355$ nm) of $C_{60}(OH)_{18}$ in aqueous solution yields the immediate formation of a transient singlet excited state with broad absorption in the 550–800 nm region with $\epsilon_{670nm} = 2130$ dm³ mol⁻¹ cm⁻¹. The energetically higher-lying singlet excited state transforms *via* intersystem crossing (*i.e.*, with $\tau_{1/2} = 500$ ps) to the also broadly absorbing (550–800 nm), triplet excited state. In contrast, at low solute concentration, the features of the ($*T_1 \rightarrow *T_n$) absorption differ significantly exhibiting an absorption maximum at 650 nm concomitant to a shoulder at 570 nm. The π -radical anion of fullereneol, [$C_{60}(OH)_{18}$]⁻, generated by electron transfer from hydrated electrons and (CH₃)₂C(OH) radicals, absorbs with λ_{max} at 870, 980 and 1050 nm. Based on electron transfer studies with suitable electron donor/acceptor substrates, the reduction potential of the $C_{60}(OH)_{18}/[C_{60}(OH)_{18}]^{-}$ couple was estimated to be in the range between -0.358 and -0.465 V *vs.* NHE.

The macroscopic fabrication of carbon clusters^{1,2} and the intriguing combination of prominent photosensitizer^{3,4} and electron acceptor properties^{5–8} has prompted an interdisciplinary interest in their participation in key biological processes, such as free-radical scavenging, antiviral activity, DNA cleavage, and photodynamic therapy.^{9–16} Dissolution of pristine fullerenes in aqueous media necessitates, however, incorporation of the hydrophobic fullerene moiety into amphiphilic assemblies such as cyclodextrins, calixarenes, surfactants, and vesicles.^{17–23} As a consequence of the different nature of the host/water interface, the reactivity of the C_{60} guest is strongly impacted, for example, by the charge of the polar headgroups or aromaticity of the host structure.²⁴

The development of versatile methodologies implementing the covalent functionalization of the fullerene core opened access to a broad spectrum of tailor-made fullerene derivatives with specifically designed properties.^{25–28} In particular, considerable attention focuses on promoting the water solubility, for example, of C_{60} *via* introduction of hydrophilic addends, including negatively charged carboxylic, positively charged quaternary ammonium, and non-charged ethylene glycol groups.^{29–33} Although, attachment of a single hydrophilic addend at the fullerene core enhances the water solubility noticeably, irreversible formation of fullerene clusters occurs instantaneously.^{30,31} This clustering derives presumably from the strong π - π interaction between the hydrophobic fullerene cores. Capping the surface of these derivatives with surfactants, however, was found to prevent formation of any clusters and, in turn, to stabilize fullerene monomers. Thus it is conceivable that polyfunctionalization of the fullerene's hydrophobic surface will be an alternative way to prevent aggregation. It will be demonstrated that this is indeed the case for fullereneol, $C_{60}(OH)_{18}$, a highly water soluble compound which has recently been prepared.^{34,35}

In order to assess the potential participation of $C_{60}(OH)_{18}$ in biological applications, it is of fundamental importance to understand the physico-chemical and electron transfer properties. With the objective of characterizing transient interme-

diates and stable products involving excited and reduced states of fullereneol, photochemical and radiation chemical studies of this functionalized fullerene derivative have been carried out in aqueous solutions.

Experimental

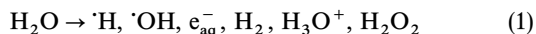
Fullerene solutions were prepared in deionized nanopure water. $C_{60}(OH)_{18}$ was synthesized at the Centre for Condensed Matter (Taiwan) following a recently reported procedure.^{34,35} All other chemicals were of analytical grade purity. Iolar grade N₂ (Indian Oxygen; 99.9% purity) was used to deaerate the samples. Steady state optical absorption and fluorescence emission spectra were recorded with a Hitachi 330 spectrophotometer and an F 4010 spectrofluorometer, respectively. Particle size determination was carried out by means of a dynamic light scattering technique using a Brookhaven Instrument Corporation particle sizer model BI-90.

Picosecond laser flash photolysis experiments were carried out either at the Notre Dame Radiation Laboratory (USA) using a mode-locked, Q-switched Quantel YG-501 DP Nd/YAG laser (18 ps; $\lambda_{ex} = 355$ nm; output 2–3 mJ pulse⁻¹) system or at the Chemistry Division, BARC, Bombay (India) using a mode-locked Nd/YAG laser (35 ps; $\lambda_{ex} = 355$ nm; 4 mJ) (Continuum, Model 501-C-10). Complementary nanosecond laser experiments were performed at the Chemistry Division, BARC, Bombay using an Nd/YAG laser (10 ns; $\lambda_{ex} = 355$ nm; 8 mJ). Transient absorption spectra were recorded with a tungsten lamp in combination with a Bausch and Lomb monochromator, Hamamatsu R 928 PMT and a 500 MHz Tektronix TDS-540A digital oscilloscope.^{36,37}

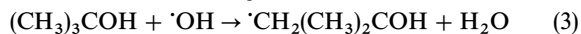
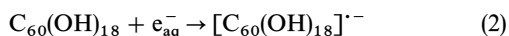
Pulse radiolytic experiments, for recording the spectra in the IR region, were carried out at the Notre Dame Radiation Laboratory utilizing 50 ns pulses of 8 MeV electrons from a Model TB-8/16-1S Electron Linear Accelerator with doses in the range 1–5 Gy pulse⁻¹. The rest of the pulse radiolysis experiments were carried out at the Chemistry Division, BARC, Bombay with high energy electron pulses (7 MeV, 50 ns, dose pulse *ca.* 15 Gy) generated from a linear electron accelerator.^{38,39}

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Radiolysis of N₂-saturated neutral aqueous solution leads to the formation of three highly reactive species ($\cdot\text{H}$, $\cdot\text{OH}$, e_{aq}^-) in addition to inert or less reactive molecular products (H_2 , H_3O^+ , H_2O_2).



The reaction of $\text{C}_{60}(\text{OH})_{18}$ with hydrated electrons (e_{aq}^-) was studied [eqn. (2)] in the presence of 2-methylpropan-2-ol (0.3 mol dm⁻³) which quantitatively scavenges the $\cdot\text{OH}$ radicals [eqn. (3)] at pH = 7.



Results and Discussion

Optical absorption and emission of $\text{C}_{60}(\text{OH})_{18}$

The ground state optical absorption of $\text{C}_{60}(\text{OH})_{18}$ in aqueous solution exhibits a strong absorption band with λ_{max} at 215 nm, accompanied by shoulders in the 230–280 and 300–360 nm region.⁴⁰ The spectrum revealed, however, a remarkable dependence on the solute concentration. In particular, a significant deviation from the Lambert–Beer law at higher solute concentrations indicates the formation of aggregates (Table 1). The ratio of absorbance $A_{300\text{nm}}/A_{500\text{nm}}$ decreases with decreasing fullerene concentration. This suggests the presence of fullerene aggregates in aqueous solution displaying the following characteristics: (i) significant broadening in the visible range of the spectrum and (ii) stronger molar absorptivity in the 300 nm region than in the 500 nm range. Dynamic light scattering, which was employed to measure the particle size distribution, corroborates this assumption, *e.g.*, the average particle size increases noticeably at higher $\text{C}_{60}(\text{OH})_{18}$ concentration (Table 1).

The emission spectrum of dilute $\text{C}_{60}(\text{OH})_{18}$ solution (2×10^{-3} mol dm⁻³) obtained upon 360 nm excitation, shows weak and broad fluorescence in the 450–700 nm region as depicted in Fig. 1. Upon increasing the solute concentration the fluorescence intensity changed, however, only insignificantly. This indicates that the fluorescence lifetime of the photoexcited fullerene core is not affected by clustering and, thus, substantiates our previous observation on picosecond resolved lifetime measurements of singlet excited states of fullerene clusters [*e.g.*, $[\text{C}_{60}\text{C}(\text{COOH})_2]_n$, $[\text{C}_{60}(\text{C}_9\text{H}_{11}\text{O}_2)(\text{COOH})]_n$, and $[\text{C}_{60}(\text{C}_4\text{H}_{10}\text{N}^+)]_n$].^{30,31} It should be noted that at higher fullerene concentrations the fluorescence peak underwent a gradual shift to the red part of the spectrum which is, at least in part, ascribed to an aggregation-induced redshift of the ground-state absorption.

Excited states of $\text{C}_{60}(\text{OH})_{18}$

Fig. 2(a) shows the transient absorption spectrum monitored immediately after a 35 ps laser pulse of an N₂-saturated $\text{C}_{60}(\text{OH})_{18}$ aqueous solution (3.85×10^{-2} mol dm⁻³). The differential spectrum exhibits a broad transition band in the 550–810 nm range lacking any distinct maximum. In analogy

Table 1 Ratio of absorbance ($A_{300\text{nm}}/A_{500\text{nm}}$) and volume average size of $\text{C}_{60}(\text{OH})_{18}$ in aqueous solution

$[\text{C}_{60}(\text{OH})_{18}]$ / 10^{-2} mol dm ⁻³	$A_{300\text{nm}}$	$A_{500\text{nm}}$	$A_{300\text{nm}}/A_{500\text{nm}}$	volume average size/nm
3.85	1.36	0.125	10.88	^a
1.84	0.65	0.06	10.83	315
0.88	0.31	0.034	9.12	82
0.31	0.11	0.02	5.5	74
0.07	0.04	0.01	4.0	^b

^a Particle size not determined because the transmission of the laser light is too low. ^b Particle size too small to be detectable by the instrument.

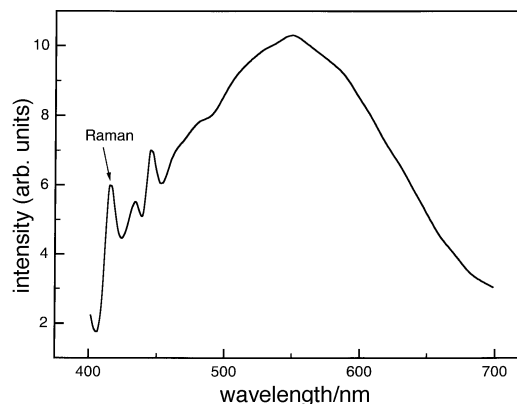


Fig. 1 Fluorescence emission of 2×10^{-3} mol dm⁻³ $\text{C}_{60}(\text{OH})_{18}$ in aqueous solution at room temperature; excitation wavelength 360 nm. The sharp peak at 415 nm is due to Raman scattering related to the water molecules.

to pristine fullerenes and various functionalized fullerene derivatives we assign this band tentatively to the fullerene's singlet–singlet ($*\text{S}_1 \rightarrow *S_n$) absorption. The molar absorption coefficient of $(^1\text{C}_{60})(\text{OH})_{18}$ at 670 nm was determined *via* comparison with that of (³benzophenone) at 525 nm ($\epsilon_{525\text{nm}} = 6500 \pm 400$ dm³ mol⁻¹ cm⁻¹) formed upon photoexcitation of benzophenone (*e.g.*, with the same ground state absorbance at 355 nm and laser fluence).^{41,42} Accordingly, the molar absorption coefficient of the ($*\text{S}_1 \rightarrow *S_n$) absorption at 670 nm was determined to be 2130 ± 300 dm³ mol⁻¹ cm⁻¹, much lower than that of pristine $(^1\text{C}_{60})$ in benzene ($\epsilon_{885\text{nm}} = 6300$ dm³ mol⁻¹ cm⁻¹).³⁷ The transient ($*\text{S}_1 \rightarrow *S_n$) absorption decayed on the picosecond timescale (inset to Fig. 2) reaching a plateau value after *ca.* 2000 ps. This decrease in absorbance can be ascribed to intersystem crossing of the singlet excited state [$(^1\text{C}_{60})(\text{OH})_{18}$] to the energetically lower lying triplet excited state [$(^3\text{C}_{60})(\text{OH})_{18}$] with $\tau_{1/2} \approx 500$ ps.

The transient absorption spectrum, 2000 ps after the laser pulse, shows a broad band with λ_{max} around 650 nm [Fig. 2(b)] which is attributable to the triplet–triplet ($*\text{T}_1 \rightarrow *T_n$) absorption of $\text{C}_{60}(\text{OH})_{18}$. Complementary nanosecond flash photolytic experiments were conducted using the same solute concentration as in the picosecond studies (3.85×10^{-2} mol dm⁻³). The transient absorption spectrum recorded 200 ns after the laser pulse is displayed in Fig. 3(a) and its broad

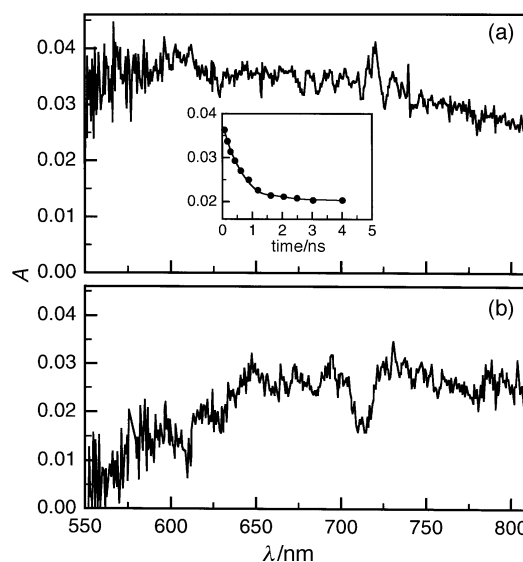


Fig. 2 Transient optical absorption spectrum observed following picosecond flash photolysis at 355 nm of $\text{C}_{60}(\text{OH})_{18}$ in N₂-saturated aqueous solution (a) immediately and (b) 1000 ps after the 18 ps laser pulse. Inset shows the decay of the transient absorption at 670 nm as a function of time.

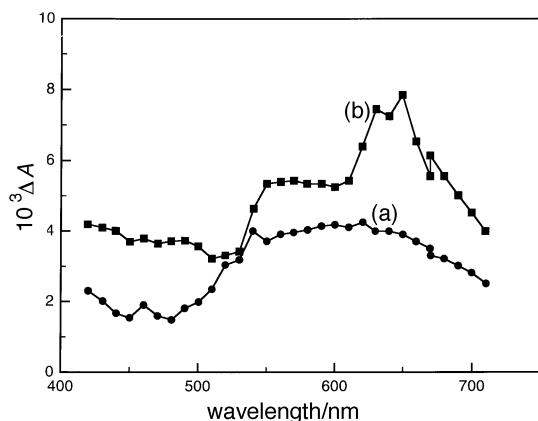


Fig. 3 Differential absorption spectra obtained upon flash photolysis at 355 nm of (a) $5.8 \times 10^{-2} \text{ mol dm}^{-3} \text{ C}_{60}(\text{OH})_{18}$ and (b) $7.5 \times 10^{-3} \text{ mol dm}^{-3} \text{ C}_{60}(\text{OH})_{18}$ in N_2 -saturated aqueous solution

absorption in the 530–700 nm range closely resembles the features recorded during the picosecond time regime.

In contrast, applying a lower solute concentration ($0.75 \times 10^{-2} \text{ mol dm}^{-3}$) in the flash photolysis experiment, the transient absorption spectrum, as typically recorded 200 ns after excitation, exhibits a broad absorption with a maximum at ca 650 nm, accompanied by a shoulder at 570 nm and a weaker band < 500 nm [Fig. 3(b)]. In line with the above described deviation of the absorbance *vs.* concentration plot from the Lambert–Beer law, these spectral differences can be rationalized in terms of reflecting the formation of fullerene aggregates at higher solute concentration. Nanosecond studies on fullerene clusters {*e.g.*, $[\text{C}_{60}\text{C}(\text{COOH})_2]_n$, $[\text{C}_{60}(\text{C}_9\text{H}_{11}\text{O}_2)(\text{COOH})]_n$, and $[\text{C}_{60}(\text{C}_4\text{H}_{10}\text{N}^+)]_n$ }, which revealed noticeable differences between monomeric and colloidal derivatives for the maximum of the corresponding ($*\text{T}_1 \rightarrow *T_n$) absorptions, further substantiates our assumption.⁴³ These studies demonstrate, furthermore, that aggregation invoked remarkable changes with respect to the decay of the fullerene's excited triplet state. Accordingly, the decay kinetics of the ($*\text{T}_1 \rightarrow *T_n$) absorption were carefully analyzed at various fullerene concentrations. Indeed, the associated decay kinetics followed a two-exponential fit (Fig. 4). While the lifetime of the longer component, typically in the range of $40 \pm 2 \mu\text{s}$, was found to be concentration independent, the lifetime of the shorter component was impacted strongly by the solute concentration. The lifetime of the shorter component decreased from $4.1 \pm 0.2 \mu\text{s}$ $\{[\text{C}_{60}(\text{OH})_{18}] = 7.5 \times 10^{-2} \text{ mol dm}^{-3}\}$ [Fig. 4(a)] to $2.5 \pm 0.2 \mu\text{s}$ $\{[\text{C}_{60}(\text{OH})_{18}] = 1.5 \times 10^{-2} \text{ mol dm}^{-3}\}$ [Fig. 4(c)]. This suggests that the slower decaying component may result from the monomeric form of $\text{C}_{60}(\text{OH})_{18}$, while the faster one may rep-

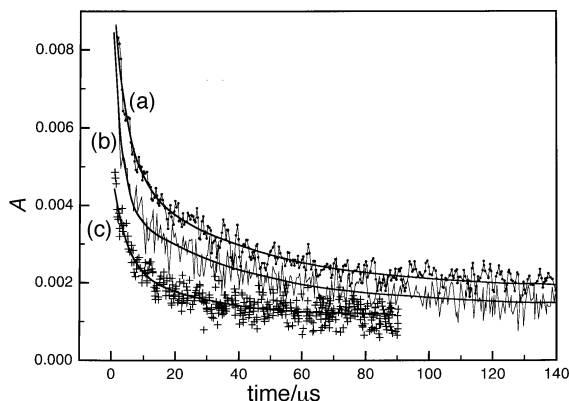
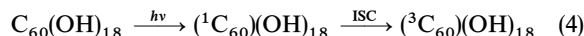


Fig. 4 The decay of the triplet excited state formed upon flash photolysis at 355 nm of aqueous solutions of $\text{C}_{60}(\text{OH})_{18}$; (a) 7.5×10^{-2} ; (b) 3.8×10^{-2} and (c) $1.5 \times 10^{-2} \text{ mol dm}^{-3}$ [recorded with the laser system at Chemistry Division, BARC, Bombay (India)]

resent the decay of $[(^3\text{C}_{60}(\text{OH})_{18})_n]$ aggregates. It should be noted that the lifetime of the presumed monomeric form of $\text{C}_{60}(\text{OH})_{18}$ is in very good agreement with various water-soluble bis-functionalized fullerene derivatives. Finally, rapid and quantitative quenching of the transient absorption in the presence of oxygen supports its origination from the triplet excited state of $\text{C}_{60}(\text{OH})_{18}$.

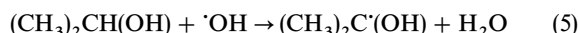


The insolubility of $\text{C}_{60}(\text{OH})_{18}$ in benzene or any other non-aqueous solvent prevented energy transfer studies by means of employing either the laser flash photolysis or pulse radiolysis technique, determination of the molar absorption coefficient of the ($*\text{T}_1 \rightarrow *T_n$) absorption, and estimation of the quantum yield of the triplet excited state formation.

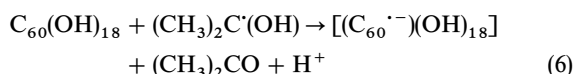
Electron transfer reactions of $\text{C}_{60}(\text{OH})_{18}$

Earlier pulse radiolytic studies have shown that hydrated electrons reduce $\text{C}_{60}(\text{OH})_{18}$ with a bimolecular rate constant of $4.5 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.⁴⁰ The transient absorption of $[(\text{C}_{60}^{\cdot-})(\text{OH})_{18}]$, as typically monitored after complete decay of the hydrated electron (*ca.* 10 μs), revealed significant features throughout the UV–VIS range. In the present investigation optical detection of the $[(\text{C}_{60}^{\cdot-})(\text{OH})_{18}]$ species, evolving from e_{aq}^- -induced electron transfer, has been extended to the near-IR range, a spectral region where π -radical anions of fullerenes [*e.g.*, $(\text{C}_{60})^{\cdot-}$, $(\text{C}_{70})^{\cdot-}$, $(\text{C}_{76})^{\cdot-}$, *etc.*] display characteristic absorptions.^{44–46} The latter have been proposed to serve as selective markers for the identification of reduced fullerene moieties in electron transfer processes. Fig. 5 shows the transient optical absorption spectrum obtained 10 μs after the electron pulse of an N_2 -purged, aqueous $\text{C}_{60}(\text{OH})_{18}$ solution containing 0.3 mol dm^{-3} 2-methylpropan-2-ol. It exhibits absorption bands at 870, 980 and 1050 nm.

The $[(\text{C}_{60}^{\cdot-})(\text{OH})_{18}]$ yield was further increased upon substitution of 2-methylpropan-2-ol by propan-2-ol (5 vol.%), as illustrated in Fig. 6. $(\text{CH}_3)_2\text{C}^{\cdot}(\text{OH})$ radicals, which evolve from $\cdot\text{OH}$ -induced hydrogen atom abstraction of propan-2-ol (eqn. 5)



are strong reductants and, accordingly, reduce $\text{C}_{60}(\text{OH})_{18}$, resulting in the formation of $[(\text{C}_{60}^{\cdot-})(\text{OH})_{18}]$. The spectral identity between the species following reduction by the hydrated electron and electron transfer from $(\text{CH}_3)_2\text{C}^{\cdot}(\text{OH})$ radicals further substantiates our spectral assignment (Fig. 5).



Electron transfer reactions with suitable redox couples were performed to determine the first reduction potential of

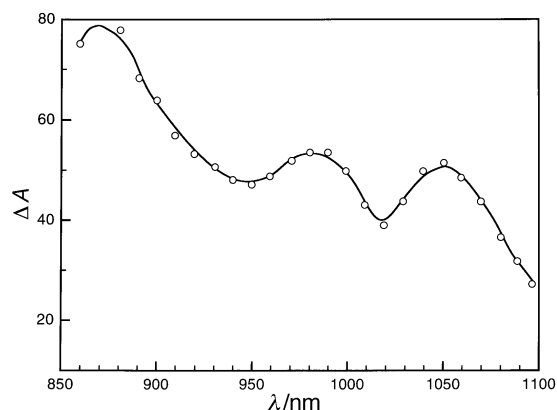


Fig. 5 Transient absorption spectrum (near-IR) of $[(\text{C}_{60}^{\cdot-})(\text{OH})_{18}]$ obtained upon pulse radiolysis of $2 \times 10^{-3} \text{ mol dm}^{-3} \text{ C}_{60}(\text{OH})_{18}$ in N_2 -saturated aqueous solution, 10 μs after the electron pulse

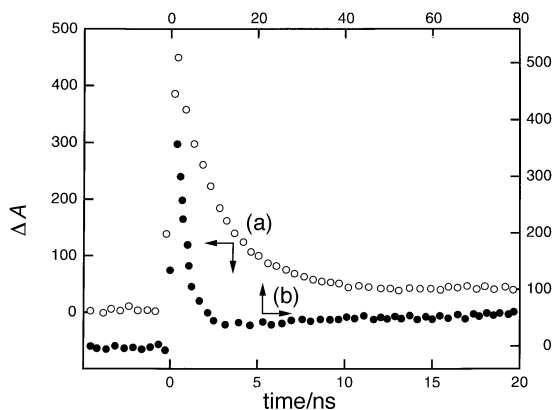
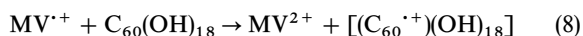
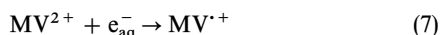


Fig. 6 Decay of the $[(C_{60}^{\bullet-})(OH)_{18}]$ transient signal at 990 nm obtained upon pulse radiolysis of 2×10^{-3} mol dm^{-3} $C_{60}(OH)_{18}$ in N_2 -saturated aqueous solution (a) (○) in the presence of 5 vol.% propan-2-ol and (b) (●) in the presence of 2-methylpropan-2-ol (0.3 mol dm^{-3})

$C_{60}(OH)_{18}$. The redox couple of methylviologen ($MV^{2+}/MV^{\bullet+}$) has a reduction potential of -0.465 V *vs.* NHE similar to that of pristine C_{60} . The strong absorption of reduced $MV^{\bullet+}$ with λ_{max} at 605 nm ($\epsilon_{605nm} = 12\,800$ dm^3 mol^{-1} cm^{-1}) is beneficial for spectrophotometrically monitoring the electron transfer processes to MV^{2+} .^{47,48} Accordingly, the electron transfer from $[(C_{60}^{\bullet-})(OH)_{18}]$ was observed *via* the decay of the fullerene's π -radical anion absorption and the simultaneous growth of the characteristic $MV^{\bullet+}$ maximum at 605 nm. Pulse radiolytic studies of N_2 -saturated $C_{60}(OH)_{18}$ solutions (1×10^{-3} mol dm^{-3} ; 0.3 mol dm^{-3} 2-methylpropan-2-ol) in the presence of low concentrations of MV^{2+} (0.1 – 1) $\times 10^{-5}$ mol dm^{-3} did not show any spectral evidence indicating the formation of the $MV^{\bullet+}$ absorption at 605 nm. This observation suggests the absence of electron transfer from the reduced fullerene derivative to methylviologen. On the other hand, the decay of the radiolytically formed $MV^{\bullet+}$ (1×10^{-3} mol dm^{-3} MV^{2+} ; 0.3 mol dm^{-3} 2-methylpropan-2-ol, $\lambda_{max} = 605$ nm) [eqn. (7)] was found to be accelerated on addition of $C_{60}(OH)_{18}$ in the range $(1$ – $8) \times 10^{-5}$ mol dm^{-3} [eqn. (8)]. The observed rate, as determined from the decay of $MV^{\bullet+}$, was linearly dependent on the fullerene concentration yielding a bimolecular rate constant of $k_8 = 1.2 \times 10^8$ dm^3 mol^{-1} s^{-1} . These studies suggest that the reduction potential of the $C_{60}(OH)_{18}/[(C_{60}^{\bullet-})(OH)_{18}]$ couple is smaller than the $MV^{2+}/MV^{\bullet+}$ couple. Similarly, the radical anion of phenolphthalein with λ_{max} at 500 nm (phenph/phenph $^{\bullet-}$ $E_{1/2} = -0.85$ *vs.* NHE)^{48,49} was also observed to display a faster decay upon $C_{60}(OH)_{18}$ addition. The bimolecular rate constant for the electron transfer from phenph $^{\bullet-}$ to $C_{60}(OH)_{18}$ was 4.5×10^8 dm^3 mol^{-1} s^{-1} (see Table 2).



The decay of the π -radical anion absorption of *p*-nitroacetophenone (*p*-NAP $^{\bullet-}$) at 550 nm formed by pulse radiolysis in an N_2 -saturated aqueous solution of 1×10^{-3} mol dm^{-3}

Table 2 Bimolecular rate constant for electron transfer from specific one-electron reductants to $C_{60}(OH)_{18}$

redox couple	$E_{1/2}/V$ <i>vs.</i> NHE	bimolecular rate constant with $C_{60}(OH)_{18}$ $/dm^3$ mol^{-1} s^{-1} ^b
$MV^{2+}/MV^{\bullet+}$ ^a	-0.465	1.2×10^8
phenph/phenph $^{\bullet-}$ ^a	-0.85	4.5×10^8
<i>p</i> -NAP/ <i>p</i> -NAP $^{\bullet-}$ ^a	-0.358	no reaction

^a Concentration of one-electron reductant: 1.0×10^{-3} mol dm^{-3} ;

^b Fullerene concentration: $(1$ – $8) \times 10^{-5}$ mol dm^{-3} .

p-NAP (0.3 mol dm^{-3} 2-methylpropan-2-ol) was not affected by any fullerene addition. This indicates that electron transfer from *p*-NAP $^{\bullet-}$ to $C_{60}(OH)_{18}$ is thermodynamically unfavorable, mainly due to the low reduction potential of *p*-nitroacetophenone ($E_{1/2} = -0.358$ V *vs.* NHE).^{47,48} In contrast, the transient absorption (550 nm) formed upon pulse radiolysis of N_2 -saturated $C_{60}(OH)_{18}$ solution containing 2-methylpropan-2-ol (0.3 mol dm^{-3}) increased on addition of low concentrations of *p*-NAP. This leads to the assumption that electron transfer occurs from the reduced $[(C_{60}^{\bullet-})(OH)_{18}]$ to *p*-NAP. The small increase in the absorbance, however, prevented an accurate determination of the bimolecular rate constant. In conclusion, these redox studies suggest that the reduction potential of the $C_{60}(OH)_{18}/[(C_{60}^{\bullet-})(OH)_{18}]$ couple is between -0.358 and -0.465 V *vs.* NHE.

Finally, 355 nm laser excitation of an N_2 -saturated aqueous solution of $C_{60}(OH)_{18}$ in the presence of low MV^{2+} concentration did not result in enhanced absorption at 400 nm excluding electron transfer from photoexcited $^*[C_{60}(OH)_{18}]$ to MV^{2+} with generation of the radical cation of methylviologen ($MV^{\bullet+}$).

Conclusion

In summary, polyhydroxylation of the hydrophobic C_{60} core enhances the water solubility of this carbon allotrope up to 4.0×10^{-2} mol dm^{-3} . Ground state absorptions, dynamic light scattering, excited triplet absorptions, and excited triplet lifetime measurements provide unambiguous evidence for the existence of fullerene clusters at high solute concentration. $C_{60}(OH)_{18}$ reacts, however, rapidly with hydrated electrons and $(CH_3)_2C^{\bullet}(OH)$ radicals to form the π -radical anion of fullerene, $[C_{60}(OH)_{18}]^{\bullet-}$, with characteristic absorption bands at 870, 980, and 1050 nm. From electron transfer reactions with the following redox couples: $MV^{2+}/MV^{\bullet+}$, phenph/phenph $^{\bullet-}$, and *p*-NAP/*p*-NAP $^{\bullet-}$ the first reduction potential of the $C_{60}(OH)_{18}/[(C_{60}^{\bullet-})(OH)_{18}]$ couple was calculated to be between -0.358 and -0.465 V *vs.* NHE.

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