

# Photophysics and Photochemistry of a Water-Soluble C<sub>60</sub> Dendrimer: Fluorescence Quenching by Halides and Photoinduced Oxidation of I<sup>-†</sup>

Isabelle Texier,<sup>‡</sup> Mário N. Berberan-Santos,<sup>\*‡</sup> Aleksandre Fedorov,<sup>‡</sup> Michael Brettreich,<sup>§</sup> Hubert Schönberger,<sup>§</sup> Andreas Hirsch,<sup>§</sup> Sydney Leach,<sup>||</sup> and René V. Bensasson<sup>⊥</sup>

Centro de Química-Física Molecular, Instituto Superior Técnico, 1049-001 Lisboa, Portugal, Institut für Organische Chemie, Universität Erlangen-Nürnberg, Henkestr. 42, D-91054 Erlangen, Germany, Observatoire de Paris-Meudon, CNRS UMR 8588, F-92195 Meudon, France, and Laboratoire de Biophysique, Muséum National d'Histoire Naturelle, 43 rue Cuvier, 75231 Paris Cedex, France

Received: January 19, 2001; In Final Form: March 19, 2001

Using electronic absorption spectroscopy, and steady-state and time-resolved fluorescence, we studied the singlet state properties of dendro[60]fullerene, a C<sub>60</sub> methanoderivative whose addend is a water-soluble dendrimer. Fluorescence quenching, especially by halide ions in water, was characterized at several temperatures. From a new relation for the activation energy of a diffusion-influenced reaction and from a comparison with the quenching in organic solvents, it is concluded that the quenching occurs by the external heavy-atom effect. An efficient photoinduced oxidation of iodide in aerated solutions and in the presence of a fullerene is also reported. The photoinduced oxidation mechanism exclusively involves ground-state oxygen.

## 1. Introduction

Intermolecular quenching of the triplet excited state of fullerenes by charge and electron<sup>1–4</sup> and energy<sup>5–7</sup> transfer has been extensively investigated in recent years. Quenching of the singlet excited state has received less attention,<sup>8–10</sup> in part owing to the very low fluorescence quantum yield of fullerenes.<sup>11</sup> No studies apparently exist concerning the quenching of the fluorescence of C<sub>60</sub> or of its derivatives. However, the fluorescence quenching of C<sub>70</sub> and C<sub>70</sub> derivatives by different electron donors<sup>8</sup> and by the external heavy-atom effect<sup>9,10</sup> has been reported. This last effect has also been used to obtain phosphorescence spectra of fullerenes and their derivatives.<sup>12</sup> Since the triplet formation quantum yield of these compounds is close to unity,<sup>11</sup> the enhancement observed in the phosphorescence quantum yield in the presence of heavy atoms is mainly due to an increase of the T<sub>1</sub> → S<sub>0</sub> radiative rate constant,<sup>10,11</sup> even if an enhancement of the S<sub>1</sub> → T<sub>1</sub> intersystem crossing rate constant also exists. Recently, a new potential application of the heavy-atom effect was proposed: The design of ultrafast-responding fullerene optical limiters.<sup>10</sup>

The fluorescence quenching mechanism of fullerenes by brominated and iodinated organic compounds occurs through the heavy-atom effect,<sup>9,10</sup> while in the quenching by halides the a priori choice between an electron-transfer mechanism and an heavy-atom effect is not clear-cut.<sup>13</sup>

The initial objectives of the present work were (1) to study the efficiency of fluorescence quenching of C<sub>60</sub> derivatives by halogenated compounds and halides in polar solvents, including water, (2) to determine to which extent the type and number of addends influence the response to quenching of the C<sub>60</sub> core,

and (3) to establish the mechanism of fluorescence quenching of fullerenes by halides in aqueous solutions.

For these purposes, we investigated the fluorescence properties of a methanofullerene whose addend is a water-soluble dendrimer (Scheme 1).

This compound, referred to as “dendro[60]fullerene” in the following, is particularly interesting, owing to its 18 carboxylic acid groups, which allow easy solubilization in water at pH 7.4. It is then possible to study the fluorescence quenching of the fullerene core by halides in a polar medium, known to favor the separation of the reactants pair after electron transfer. The fluorescence properties of this C<sub>60</sub> monoadduct dendro[60]-fullerene were compared to those of a monoadduct C<sub>60</sub>[C(CO<sub>2</sub>Et)<sub>2</sub>] in toluene and to those of a tris-adduct C<sub>60</sub>[C(CO<sub>2</sub>H)<sub>2</sub>]<sub>3</sub> in water to check the influence of the number and nature of the addend and that of the solvent. The fluorescence quenching results include the temperature dependence of the rate constants. A relation for the activation energy of a diffusion-influenced reaction is derived and is used to analyze the experimental results.

In the course of the studies, an efficient photoinduced oxidation of iodide was discovered, and its characterization is also the subject of the present work. Two mechanisms for the photoinduced oxidation of iodide are in principle possible: type I, which involves only ground-state oxygen (<sup>3</sup>O<sub>2</sub>) and has as a first step the reaction between triplet sensitizer (fullerene) and substrate (iodide), and type II, whose first step is the reaction between triplet sensitizer and ground-state oxygen (<sup>3</sup>O<sub>2</sub>) to produce singlet oxygen (<sup>1</sup>O<sub>2</sub>).

## 2. Experimental Section

The dendro[60]fullerene<sup>14</sup> was synthesized according to procedures described elsewhere,<sup>14–18</sup> as well as C<sub>60</sub>[C(CO<sub>2</sub>Et)<sub>2</sub>] and C<sub>60</sub>[C(CO<sub>2</sub>H)<sub>2</sub>]<sub>3</sub> (all addends equatorial).<sup>15–18</sup> C<sub>60</sub> (>99%) was obtained from Stefan Kaesdorf (Munich, Germany). Toluene (spectroscopic grade, Merck) and ethanol (spectroscopic grade, Aldrich) were used as supplied. Millipore bidistilled water

<sup>†</sup> This work was presented at the PP2000 in Costa do Estoril, Portugal, honoring Professor Ralph Becker's contributions.

\* Corresponding author. E-mail: berberan@ist.utl.pt.

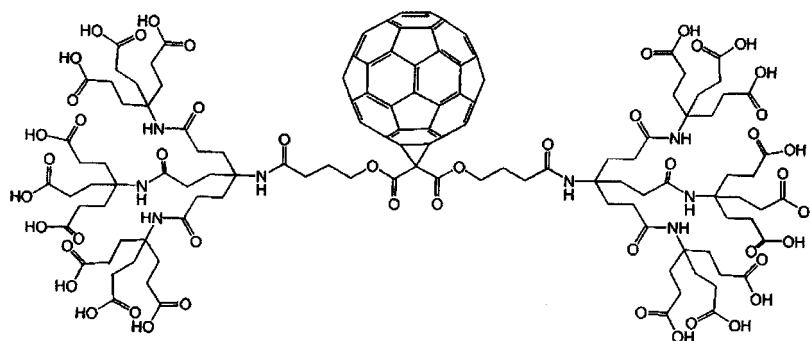
<sup>‡</sup> Instituto Superior Técnico.

<sup>§</sup> Universität Erlangen-Nürnberg.

<sup>||</sup> Observatoire de Paris-Meudon.

<sup>⊥</sup> Muséum National d'Histoire Naturelle

## SCHEME 1: Dendro[60]fullerene Structure



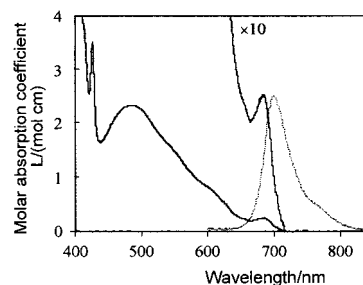
or deuterated water (Aldrich, 99%), the pH of which were adjusted to 7.4, were used for the experiments performed in aqueous solvents. The usual dendro[60]fullerene concentration was  $4\text{--}6 \times 10^{-5} \text{ mol L}^{-1}$ , and the solutions were aerated ( $[\text{O}_2] = 3 \times 10^{-4} \text{ mol L}^{-1}$ ), unless specified otherwise. Cyclohexyl iodide (Aldrich, 98%), bromobenzene (Riedel de Haën, 98%), sodium iodide (Aldrich, 99.999%), cesium iodide (Aldrich, 99.9%), potassium bromide (Riedel, spectroscopic purity), and cesium chloride (Aldrich, >99.999%) were used as supplied.

Absorption spectra were recorded on a Shimadzu 3101PC UV-vis-NIR spectrophotometer and fluorescence spectra on a Spex Fluorolog 112 or a SLM 8000C spectrofluorimeter. The fluorescence quantum yields were determined from corrected spectra, using  $\text{C}_{60}$  in toluene as a standard<sup>11b</sup> ( $\Phi = 3.2 \times 10^{-4}$ ). For the quenching experiments, the excitation wavelength was usually 480 nm, and instrumental bandwidths were 18 nm on the excitation and 4.5 nm on the emission. Temperature control was within  $\pm 0.5 \text{ }^\circ\text{C}$ . The 150 W xenon lamp of the Spex Fluorolog 112 spectrofluorimeter was also used for the irradiation experiments described in section 3.3. In the configuration used (instrumental excitation bandwidths of 18 nm, fluorescence cell of 5 mm width, and 5 mm optical path length), the incident photon flux on the fluorescence cell, measured with a calibrated photodiode, was  $2.00 \times 10^{-7} \text{ einstein min}^{-1}$  at 490 nm. This flux was very stable after the lamp had been switched on for more than 30 min.

Time-resolved picosecond fluorescence measurements were performed using the single-photon timing method with laser excitation. The setup consisted of a mode-locked Coherent Innova 400-10 argon-ion laser that synchronously pumped a cavity dumped Coherent 701-2 dye (Rhodamine 6G) laser, delivering 3–4 ps pulses (with ca. 40 nJ/pulse) at a frequency of 3.4 MHz. Intensity decay measurements were made by an alternate collection of impulse and decay, with the emission polarizer set at the magic angle position. Impulse was recorded slightly away from the excitation wavelength with a scattering suspension. For the decays, a cutoff filter was used, effectively removing all excitation light. The emission signal passed through a depolarizer, a Jobin-Yvon HR320 monochromator with a grating of 100 lines/nm, and was recorded on a Hamamatsu 2809U-01 microchannel plate photomultiplier as a detector. A time scale of 2.75 ps/channel was used. The instrument response function had an effective fwhm of 35 ps. Usually no less than 5000 counts were accumulated at the maximum channel.

### 3. Results

**3.1. Absorption and Fluorescence of the Dendro[60]-fullerene.** The visible absorption spectrum of the dendro[60]-fullerene in water is displayed in Figure 1. An identical spectrum is observed in ethanol.



**Figure 1.** Absorption spectrum (full line) and emission spectrum (dashed line) of the dendro[60]fullerene in water.

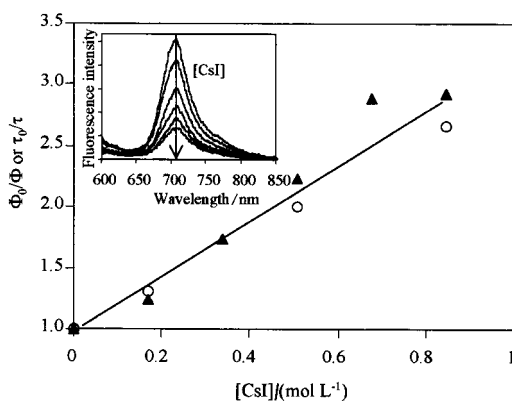
Absorption maxima occur at 689 nm (weak band,  $\epsilon = 230 \text{ L mol}^{-1} \text{ cm}^{-1}$ ), 470 nm (broad band,  $\epsilon = 2460 \text{ L mol}^{-1} \text{ cm}^{-1}$ ), 426 nm (sharp peak,  $\epsilon = 3850 \text{ L mol}^{-1} \text{ cm}^{-1}$ ), 325 nm ( $\epsilon = 40\,900 \text{ L mol}^{-1} \text{ cm}^{-1}$ ), and 257 nm ( $\epsilon = 114\,000 \text{ L mol}^{-1} \text{ cm}^{-1}$ ). The absorption onset occurs at ca. 720 nm. The recorded absorption spectrum is similar to those reported for other  $\text{C}_{60}$  monoderivatives:<sup>11b,19–26</sup> It is broader and extends to longer wavelengths than that of  $\text{C}_{60}$  and shows the same characteristic sharp peak at  $\sim 430 \text{ nm}$ , absent in  $\text{C}_{60}$ .<sup>20</sup> The determined molar absorption coefficients are in good agreement with reported values.<sup>12b,19–26</sup> Like other  $\text{C}_{60}$  monoderivatives, the dendro[60]-fullerene is a stronger absorber in the visible region than that in  $\text{C}_{60}$ , as a result of symmetry reduction.<sup>11b,19–26</sup>

The fluorescence spectrum of the dendro[60]fullerene in water is also shown in Figure 1. As for the absorption spectrum, no difference is observed between water and ethanol. The fluorescence spectrum peaks at 702 nm and is narrower than that of  $\text{C}_{60}$ , with a second and weaker vibronic band at longer wavelengths. A blue shift of the maximum upon cooling was observed. The 702 nm peak is a mirror image of the 0–0 absorption band at 689 nm, as shown in Figure 1.

The determined fluorescence quantum yield,  $\Phi = (4.0 \pm 0.4) \times 10^{-4}$ , and fluorescence lifetime,  $\tau = 1.45 \pm 0.1 \text{ ns}$ , are only slightly higher than those of  $\text{C}_{60}$  ( $\Phi = 3.2 \times 10^{-4}$ ,  $\tau = 1.1 \text{ ns}$ <sup>11b</sup>). The fluorescence quantum yield, in particular, remains low, while for some  $\text{C}_{60}$  pyrrolidine derivatives, the fluorescence quantum yield is reported to attain  $2 \times 10^{-2}$ .<sup>23,24</sup> This difference in behavior is attributed to a strong charge-transfer electronic interaction of the  $\text{C}_{60}$  core with the addend in these compounds, affecting many of their properties, including acidity. This kind of addend–core interaction is negligible in the derivatives studied here. The experimental radiative rate constant ( $2.3\text{--}2.7 \times 10^5 \text{ s}^{-1}$ ) obtained for the dendro[60]fullerene is in good agreement with the calculated value,  $2.5\text{--}2.7 \times 10^5 \text{ s}^{-1}$ , using the Strickler–Berg equation,<sup>27</sup> and it is similar to that of  $\text{C}_{60}$  ( $2.9 \times 10^5 \text{ s}^{-1}$ ). The small increase of the fluorescence lifetime of the dendro[60]fullerene in comparison to that of  $\text{C}_{60}$  is thus mainly due to a decrease in the radiationless rate constant.

**TABLE 1: Stern–Volmer and Quenching Bimolecular Rate Constants Obtained for the Dendro[60]fullerene and Other C<sub>60</sub> Methanoderivatives at Room Temperature (295 K)**

C <sub>60</sub> derivative	solvent	quencher	K <sub>SV</sub> (L mol <sup>-1</sup> )	k <sub>q</sub> (L mol <sup>-1</sup> s <sup>-1</sup> )	k <sub>q</sub> dependence with T
C <sub>60</sub> [C(CO <sub>2</sub> Et) <sub>2</sub> ]	toluene	bromobenzene	0.27 ± 0.05	(1.9 ± 0.4) × 10 <sup>8</sup>	no
dendro[60]fullerene	ethanol	bromobenzene	0.22 ± 0.05	(1.5 ± 0.4) × 10 <sup>8</sup>	no
dendro[60]fullerene	ethanol	cyclohexyliodide	4.7 ± 0.5	(3.3 ± 0.3) × 10 <sup>9</sup>	—
dendro[60]fullerene	water <sup>a</sup>	CsI	2.5 ± 0.2	(1.7 ± 0.2) × 10 <sup>9</sup>	yes
dendro[60]fullerene	water <sup>a</sup>	NaI	2.5 ± 0.2	(1.7 ± 0.2) × 10 <sup>9</sup>	—
dendro[60]fullerene	water <sup>a</sup>	KBr	0.35 ± 0.1	(2.4 ± 0.7) × 10 <sup>8</sup>	—
dendro[60]fullerene	water <sup>a</sup>	CsCl	0	0	—
C <sub>60</sub> [C(CO <sub>2</sub> H) <sub>2</sub> ] <sub>3</sub>	water <sup>a</sup>	CsI	4 ± 1	(1.6 ± 0.5) × 10 <sup>9</sup>	—
C <sub>60</sub> [C(CO <sub>2</sub> H) <sub>2</sub> ] <sub>3</sub>	water <sup>a</sup>	NaI	5 ± 1	(2.0 ± 0.5) × 10 <sup>9</sup>	—

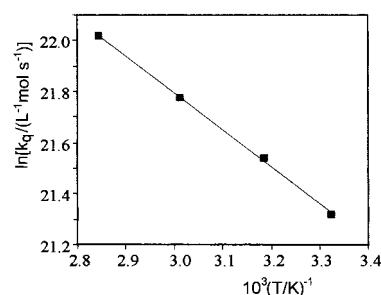
<sup>a</sup> pH 7.4.**Figure 2.** Stern–Volmer plots for the quenching by cesium iodide of the fluorescence quantum yield (triangles) and the fluorescence lifetime (circles) of the dendro[60]fullerene in water. Insert: Fluorescence spectra of the dendro[60]fullerene in the presence of increasing concentrations of CsI.

**3.2. Fluorescence Quenching.** The fluorescence spectrum of the dendro[60]fullerene in water, in the presence of an increasing concentration of CsI, is displayed in the insert of Figure 2.

The fluorescence is efficiently quenched, as shown by the Stern–Volmer plots also presented in Figure 2, obtained from measurements of both the fluorescence quantum yield and the fluorescence lifetime as a function of quencher concentration. The Stern–Volmer constants derived from the steady-state and time-resolved measurements are identical within experimental error. The Stern–Volmer constants  $K_{SV}$  and the bimolecular fluorescence quenching rate constants  $k_q$  for several quenchers in water and in ethanol at room temperature are collected in Table 1.

Quenching values determined for two other C<sub>60</sub> methano derivatives, C<sub>60</sub>[C(CO<sub>2</sub>Et)<sub>2</sub>] in toluene ( $\tau = 1.45$  ns<sup>25,26</sup>) and C<sub>60</sub>[C(CO<sub>2</sub>H)<sub>2</sub>]<sub>3</sub> (eee) in water ( $\tau = 2.45$  ns<sup>25,26</sup>) are also reported for comparison. The important uncertainties associated with these values, especially in the case of C<sub>60</sub>[C(CO<sub>2</sub>H)<sub>2</sub>]<sub>3</sub>, are due to the very weak fluorescence signals.

From the results displayed in Table 1, it can be noticed that for a given quencher, the quenching rate constants  $k_q$  are very similar for all the studied C<sub>60</sub> derivatives. The functionalization pattern and the nature of the addends are therefore of secondary importance. From the Stokes–Einstein and Debye equations, the diffusion-limited quenching rate constants in water are estimated to be  $7 \times 10^9$  L mol<sup>-1</sup> s<sup>-1</sup> for a neutral fullerene,  $4 \times 10^9$  L mol<sup>-1</sup> s<sup>-1</sup> for a fullerene bearing a single negative charge,  $2 \times 10^9$  L mol<sup>-1</sup> s<sup>-1</sup> for a fullerene bearing two negative charges, and  $1 \times 10^9$  L mol<sup>-1</sup> s<sup>-1</sup> for a fullerene bearing three negative charges, using a fullerene radius of 5.0 Å<sup>28</sup> and a radius of 2.2 Å for the I<sup>-</sup> ion.<sup>29</sup> It is difficult to evaluate the effective

**Figure 3.** Influence of the temperature on the bimolecular rate constant of quenching of the dendro[60]fullerene by cesium iodide in water.

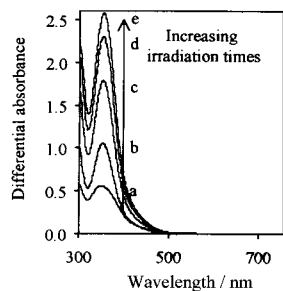
negative charge of the fullerene derivatives in water, especially that of the dendro[60]derivative. Even if the 18 carboxylic groups are deprotonated at pH 7.4, the effective negative charge for the C<sub>60</sub> core should be low, since the long chains of the addend make it very diffuse. In ethanol, the estimated diffusion-limited quenching rate constant is  $6 \times 10^9$  L mol<sup>-1</sup> s<sup>-1</sup>. From the above calculations, it can be concluded that the observed bimolecular quenching rate constants obtained for the fullerenes in the presence of the most effective quenchers, iodide and iodine compounds, are close to but slightly lower than the limiting values for ideal spherical particles reacting at contact under diffusion control.

The data concerning the halide salts in water (Table 1) show that the quenching is mainly due to the halide anion, since no difference in the constants is observed between sodium and cesium iodide, in the cases of both the dendro[60]fullerene and C<sub>60</sub>[C(CO<sub>2</sub>H)<sub>2</sub>]<sub>3</sub> and that no quenching of the dendro[60]fullerene occurs in the presence of cesium chloride.

The temperature dependence of the bimolecular rate constant was studied for some quenchers. For cesium iodide, a significant increase of quenching with temperature occurs. The corresponding Arrhenius plot is shown in Figure 3 for the dendro[60]fullerene. The calculated activation energy is  $12 \pm 2$  kJ mol<sup>-1</sup>.

For the weaker quencher, bromobenzene, no temperature effect was observed either for the dendro[60]fullerene in ethanol or for C<sub>60</sub>[C(CO<sub>2</sub>Et)<sub>2</sub>] in toluene.

**3.3. Products Formed under Irradiation in the Presence of Iodide in Aerated Aqueous Solution.** During the fluorescence quenching studies, the formation of a colored product was observed under certain conditions when iodine salts (Na and Cs) were used. In the absence of oxygen (sealed cell under vacuum), careful analysis of the fluorescence and absorption spectra did not show any modification, even for long irradiation times. However, in the presence of oxygen (aerated solution), a progressive yellowing of the solution, accompanied by the appearance of an absorption band at 353 nm, occurs in a matter of minutes upon continuous irradiation with the fluorimeter excitation beam. This observation was not reported in previous



**Figure 4.** Differential absorption spectra obtained during the irradiation of an aqueous solution of dendro[60]fullerene ( $5.3 \times 10^{-5} \text{ mol L}^{-1}$ ) in the presence of sodium iodide ( $0.60 \text{ mol L}^{-1}$ ). A differential spectrum represents the difference between the spectrum obtained at a defined time of irradiation and the spectrum of the solution before irradiation. (a) 3 min of irradiation, (b) 9 min of irradiation, (c) 15 min of irradiation, (d) 21 min of irradiation, and (e) 27 min of irradiation.

studies of excited states of fullerenes in the presence of iodide, probably because the concentrations of  $\text{I}^-$  used were always much lower than those of the present study.

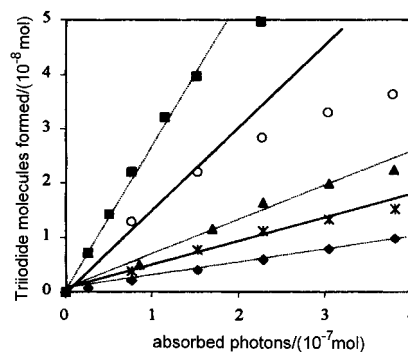
The absorption peak at 353 nm is characteristic of  $\text{I}_3^-$ , an oxidation product of  $\text{I}^-$ .  $\text{I}_3^-$  is not formed during the irradiation of an  $\text{I}^-$  solution in the same conditions but without the dendro[60]fullerene derivative. On the other hand, the Stern–Volmer constants are the same in the absence and presence of oxygen. This shows that the singlet quenching process is not directly affected by the presence of oxygen, as expected since the singlet lifetime is too short and oxygen concentration too low (the solubility of oxygen is ca.  $3 \times 10^{-4} \text{ mol L}^{-1}$  at room temperature and atmospheric conditions) for this state to be efficiently quenched by  $\text{O}_2$ . The presence of oxygen only affects the evolution of the products following the quenching process.

A close analysis of the absorption and fluorescence spectra of the solutions during irradiation does not show any modification other than the appearance of the 353 nm band. The possible presence of the fullerene radical anion, which possesses a strong NIR absorption band at 1020 nm,<sup>30</sup> or of other products emitting or absorbing in the visible and near UV was not detected. The NIR band of the fullerene radical anion was already observed in the case of the reduction of water-solubilized  $\text{C}_{60}$  (in the presence of surfactants or  $\gamma$ -cyclodextrins), occurring by quenching of the triplet excited state by electron transfer.<sup>2,3</sup> The absorption coefficients of  $\text{I}_3^-$  at 353 nm ( $26\,400 \text{ L mol}^{-1} \text{ cm}^{-1}$ )<sup>31</sup> and that of the dendro[60]fullerene radical anion at 1020 nm ( $7400 \text{ L mol}^{-1} \text{ cm}^{-1}$ )<sup>30</sup> are on the same order of magnitude. However, the dendro[60]fullerene radical anion has a lifetime of 53 ms in water<sup>30</sup> and is efficiently quenched by oxygen<sup>30</sup> and  $\text{I}^-$ . Its stationary concentration in our experimental conditions can be estimated to be several orders of magnitude below the detection limit. The eventual formation of the fullerene anion would only be seen in nanosecond flash photolysis experiments with much higher irradiation fluences.

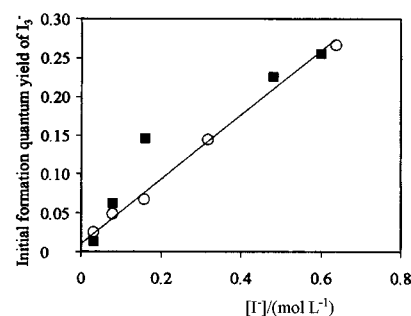
The evolution of the number of moles of  $\text{I}_3^-$  against the number of moles of photons absorbed in aqueous aerated solutions of dendro[60]fullerene containing different initial concentrations of iodide is shown in Figure 5.

These plots are linear for irradiation times that are not too long. For long times, the rate of production of  $\text{I}_3^-$  slows down but remains noticeable. The quantum yield of  $\text{I}_3^-$  formation is plotted against the initial concentration of iodide, in both normal and heavy (deuterated) water, in Figure 6.

These two solvents differ by the intrinsic lifetime of singlet oxygen ( $4.2 \mu\text{s}$  in  $\text{H}_2\text{O}$ ,  $55.0 \mu\text{s}$  in  $\text{D}_2\text{O}$ ).<sup>32</sup> It can be seen that this parameter has no effect on the formation rate of  $\text{I}_3^-$ .



**Figure 5.** Evolution of the number of moles of  $\text{I}_3^-$  against the number of moles of photons absorbed for different initial iodide concentrations in aerated dendro[60]fullerene solutions in  $\text{D}_2\text{O}$ .  $[\text{I}^-] = 3.19 \times 10^{-2}$  (diamonds),  $7.98 \times 10^{-2}$  (stars),  $1.60 \times 10^{-1}$  (triangles),  $3.19 \times 10^{-1}$  (circles), and  $6.38 \times 10^{-1}$  (squares)  $\text{mol L}^{-1}$ .



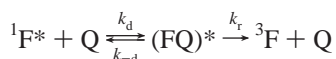
**Figure 6.** Quantum yields of formation of  $\text{I}_3^-$  against the initial concentration of iodide, in aqueous aerated solutions of dendro[60]fullerene, either in  $\text{H}_2\text{O}$  (squares) or in  $\text{D}_2\text{O}$  (circles).

## 4. Discussion

**4.1. Mechanism of Fluorescence Quenching.** The results presented clearly show the existence of dynamic quenching of the singlet excited state of  $\text{C}_{60}$  derivatives by halides. The quenching is nearly diffusion-controlled for iodinated quenchers and 1 order of magnitude lower for brominated ones. The rate constants do not change appreciably when varying the number of addends between 1 and 3, nor when going from organic solvents (toluene, ethanol) to water. To the best of our knowledge, this is the first report of the fluorescence quenching of a water-soluble  $\text{C}_{60}$  derivative, since previous quenching studies focused on the triplet excited state.<sup>1–7,11</sup> We now center on the elucidation of the quenching mechanism. In the case of bromobenzene and cyclohexyl iodide in ethanol and toluene, the quenching mechanism is likely to be the external heavy-atom effect, as has been observed for  $\text{C}_{70}$  and derivatives in halogenated solvents.<sup>9,10</sup> In the case of the aqueous halides, the fluorescence quenching rate constants increase again with the atomic number of the halide but also according to the decreasing redox potential of the couples  $\text{X}^{\cdot}/\text{X}^-$ , where  $\text{X} = \text{Br}$  or  $\text{I}$ . The fluorescence quenching could then be also due to charge or electron transfer, often observed for the quenching of the triplet excited state.<sup>1–4</sup> Nevertheless, the very similar values of the quenching rate constant obtained in toluene, ethanol, and water (Table 1) point to a similar mechanism, dependent on the halogen moiety but very little on solvent. External heavy-atom quenching is thus also a reasonable mechanism in aqueous solution. Previous evidence for this mechanism is the observed decrease of the triplet rise time in the presence of  $\text{I}^-$  ions for  $\text{C}_{60}$  solubilized in  $\gamma$ -cyclodextrin.<sup>2</sup>

We now turn to the discussion of the temperature dependence of the quenching in aqueous solutions. As will be shown, the

results provide further support for the external heavy-atom mechanism. The observed temperature dependence of the quenching rate constant can be accounted for by assuming the usual kinetic scheme for diffusion-influenced reactions



Neglecting transient effects, the overall rate constant can be written as

$$k = \frac{k_c}{1 + \frac{k_c}{k_d}} \quad (1)$$

with  $k_c = (k_d/k_{-d})k_r$ . We first consider the interaction between neutral species. Then  $k_c$  is also given by

$$k_c = V_m k_r \quad (2)$$

where  $V_m$ , the molar volume of the statistical complex  $(\text{FQ})^*$ , is the temperature-independent pseudoequilibrium constant for its formation. From the definition of activation energy

$$E_a = RT^2 \frac{d \ln k}{dT} \quad (3)$$

one obtains from eq 1 that the apparent activation energy is

$$E'_a = \frac{k}{k_d} E_d + \frac{k}{k_c} E_a \quad (4)$$

where  $E_d$  is the activation energy of  $k_d$  and  $E_a$  is the activation energy of  $k_c$ . The activation energy of the diffusional step can be obtained assuming that the rate constant for diffusion is

$$k_d = \frac{k_0 T}{\eta^\alpha} \quad (5)$$

where  $k_0$  is a numerical constant,  $\alpha \leq 1$ , and the macroscopic viscosity obeys the Andrade equation

$$\eta = \eta_0 e^{E_\eta/RT} \quad (6)$$

where  $E_\eta$  is the activation energy of fluidity; hence, using again eq 3

$$E_d = RT + \alpha E_\eta \quad (7)$$

and substituting eq 7 into eq 4, one finally obtains

$$E'_a = \frac{k}{k_d} (RT + \alpha E_\eta) + \frac{k}{k_c} E_a \quad (8)$$

For the external heavy-atom effect, no activation energy is expected for the quenching process, and eq 8 reduces to

$$E'_a = \frac{k}{k_d} (RT + \alpha E_\eta) \quad (9)$$

For relatively weak quenchers such as the brominated ones,  $k \ll k_d$ , and the apparent activation energy is zero, as observed (no temperature dependence for the quenching). On the other hand, for nearly-diffusion-controlled reactions,  $k \cong k_d$ , and the apparent activation energy approaches that of the viscosity. Note that since  $E_\eta$  is usually small (a few tens of kilojoules), the  $RT$  term cannot be neglected in general.

If the interacting species are charged, use is made of the Debye equation, which can be written as

$$k_d = \frac{k_0 T}{\eta^\alpha p} \quad (10)$$

where

$$p = \frac{\delta}{e^\delta - 1} \quad (11)$$

and

$$\delta = \frac{\left( \frac{z_F z_Q e^2}{4\pi\epsilon_0\epsilon_r R^*} \right)}{k_B T} = z_F z_Q \frac{R_0}{R^*} \quad (12)$$

where  $z_F$  is the charge of the fullerene,  $z_Q$  is the charge of the quencher,  $e$  is the electron charge,  $\epsilon_0$  is the vacuum permittivity,  $\epsilon_r$  is the dielectric constant (relative permittivity) of the solvent,  $R^*$  is the collision radius in the statistical complex,  $k_B$  is the Boltzmann constant, and  $R_0$  is a characteristic length, a function of  $\epsilon_r$  and  $T$ . The dimensionless parameter  $\delta$  is the ratio between the electrostatic potential energy of the ions at the collision distance and the average energy of thermal motion. Instead of eq 2, one now has<sup>33</sup>

$$k_c = V_m e^{-\delta} k_r \quad (13)$$

and  $k_c$  has an activation energy, even if  $k_r$  has not. The temperature dependence of the dielectric constant of liquid water is to a very good approximation given by<sup>34a</sup>

$$\epsilon_r = a e^{-bT} \quad (14)$$

From a fit to experimental data,<sup>34b</sup>  $a = 308.7$  and  $b = 4.60 \times 10^{-3} \text{ K}^{-1}$ . One obtains from eqs 3, 4, 10, 13, and 14

$$E'_a = \frac{k}{k_d} \{ [(1 - p e^\delta) b T + p e^\delta] RT + \alpha E_\eta \} + \frac{k}{k_c} \left[ \delta(1 - bT) RT + RT^2 \frac{d \ln k_r}{dT} \right] \quad (15)$$

which is the most general form of the apparent activation energy, since it encompasses the case of neutral species as well. If  $k_r$  is not activated, then using eq 1, eq 15 can be rewritten as

$$E'_a = \delta(1 - bT) RT + \frac{k}{k_d} \{ [(1 - p e^\delta) b T - \delta(1 - bT) + p e^\delta] RT + \alpha E_\eta \} \quad (16)$$

Consider now the quenching of the dendro[60]fullerene by iodide. Assuming that  $\alpha = 1$  (Stokes–Einstein–Debye behavior), eq 16 becomes

$$E'_a = \delta(1 - bT) RT + \frac{k}{k_d} \{ [(1 - p e^\delta) b T - \delta(1 - bT) + p e^\delta] RT + E_\eta \} \quad (17)$$

If the tabulated viscosity of water in the 10–30 °C range is used, the Andrade equation gives a good fit and yields  $E_\eta = 18 \text{ kJ/mol}$ . On the other hand,  $k$  at 295 K is known (Table 1),  $k =$

$(1.7 \pm 0.2) \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ . Since the apparent activation energy is also known,  $E'_a = 12 \pm 2 \text{ kJ/mol}$ , one can estimate  $\delta$  from eq 17. If neutral species are assumed ( $\delta = 0$ ), then the calculated  $E'_a$  is 5 kJ/mol, clearly too low. The best fit is obtained for  $\delta = 1.7 \pm 0.3$ , corresponding to  $k_d = (2.7 \pm 0.5) \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$  and implying a fullerene effective charge of  $z_F = -1.7 \pm 0.3$ . The effect of the uncertainty on the parameter  $\alpha$  is not critical for the conclusions. If a value as low as  $\alpha = 0.6$ , appropriate for the diffusion of the much smaller molecular oxygen molecule ( $r = 1.8 \text{ \AA}$ ) in alkanes,<sup>35</sup> is used instead of 1, a somewhat higher charge of  $z_F = -2.4 \pm 0.3$  is obtained. One may now remark that the rate constant for the quenching of the fullerene trisadduct in water by iodide (Table 1) is indeed very close to that of the dendrimer, as expected for a similar effective charge. The total charge of the trisadduct is at most 6, but the carboxylates are attached to different parts of the fullerene sphere, and the effective charge for quenching is likely to be significantly lower.

The intrinsic quenching constant  $k_c$  can also be estimated from eq 1 once  $\delta$  is known and found to be  $k_c = 4 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ . If one now inserts this value again in eq 1, together with the previously estimated value for the diffusion rate constant in ethanol,  $6 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ , a value of  $2 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$  is obtained for the global rate constant  $k$  in ethanol, in good agreement with the measured value for the quenching of the dendro[60]fullerene by cyclohexyl iodide in this solvent (Table 1). This shows that the intrinsic quenching rate is very similar for both quenchers and confirms that a common mechanism, namely, the external heavy-atom effect, is operative.

It is relevant to mention at this point that quenching of triplet fullerenes by iodide is known to occur by electron transfer (see ref 3 and the discussion below in section 4.2) and not by the heavy-atom effect. The unimolecular rate constant for electron transfer in the excited fullerene-iodide charge-transfer complex should be high for both singlet and triplet states. However, while the fast induced  $S_1 \rightarrow T_n$  intersystem crossing in the singlet exciplex was shown to favorably compete with electron transfer, the induced  $T_1 \rightarrow S_0$  intersystem crossing is a much slower process and can no longer be an efficient alternative decay channel in the triplet exciplex.

An interesting result of the fluorescence quenching studies is the lack of quenching effect of the cesium ion. It is known that this ion efficiently quenches the fluorescence of aromatic molecules by the heavy-atom effect,<sup>36</sup> albeit not as strongly as iodide (ca. 10 times less in documented cases<sup>36</sup>). For the studied fullerenes, the effect of cesium was always negligible, given that similar values of the rate constants for quenching are measured for NaI and CsI and especially since no quenching was observed with CsCl, as shown in Table 1. An explanation for the different behavior of fullerenes with respect to the cesium ion lies in their well-established electron deficient character,<sup>11</sup> which should prevent the formation of a charge-transfer complex, even a very weak one, with a hydrated cation like cesium. This charge-transfer complex is a strict requirement for external heavy-atom quenching by means of wave function mixing,<sup>37</sup> and no quenching by this ion is thus observed.

**4.2. Photosensitized Oxidation of Iodide in Aerated Aqueous Solution.** The oxidation of iodide to triiodide by dissolved oxygen in aqueous solution is a thermodynamically favored reaction,<sup>38</sup> but a very slow one at neutral pH and in the absence of catalysts.<sup>39</sup>

The role of the dendro[60]fullerene in the observed photo-induced oxidation of iodide is now discussed. The fullerenes in the triplet state are good oxidants, and the oxidation of iodide

by  ${}^3\text{C}_{60}$  has indeed been reported<sup>3</sup>

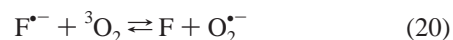


with  $k = 2 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$  for  $\text{C}_{60}$ .<sup>2,3</sup> Nevertheless, the radical anion of the fullerene recombines rapidly with the iodine radical also produced (probably already in the form  $\text{I}_2^{\bullet-}$ )<sup>3</sup> to yield a triplet state fullerene molecule (and also, with some probability, a ground-state fullerene) and  $\text{I}^-$



with  $k = 2 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$  for  $\text{C}_{60}$ ,<sup>3</sup> and no net reaction (oxidation of iodide) occurs.

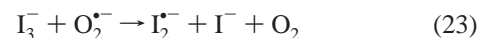
Although triplet fullerenes efficiently react with  ${}^3\text{O}_2$  to yield singlet oxygen, this reaction can be safely ruled out in our aerated solutions of iodide on the grounds of the relative concentrations of dissolved oxygen ( $[\text{O}_2] = 3 \times 10^{-4} \text{ mol L}^{-1}$ ) and iodide ( $[\text{I}^-] > 3 \times 10^{-2} \text{ mol L}^{-1}$ ). In fact, owing to the very large  $[\text{I}^-]/[\text{O}_2]$  concentration ratio (between  $10^2$  and  $2 \times 10^3$ ) and similar rate constants,<sup>2,3,40</sup> the probability of singlet oxygen formation is negligibly small. In the presence of oxygen, however, the fullerene radical anion may efficiently react (reversibly) with  $\text{O}_2$  to yield the neutral fullerene and the superoxide ion,  $\text{O}_2^{\bullet-}$ .<sup>30,41,42</sup>



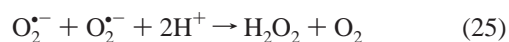
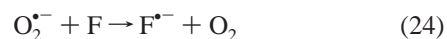
with  $k = 4 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$  for the direct reaction.<sup>30</sup> Other products are in principle possible, like polyoxygen adducts and fragmentation of the fullerene cage, but as remarked in section 3.3, no spectral evidence for this was found in our experimental conditions. Since the direct reaction removes the  $\text{F}^{\bullet-}$ , the diffusion controlled recombination of  $\text{I}^{\bullet}$  atoms (in the form  $\text{I}_2^{\bullet-}$ ) yielding  $\text{I}_3^-$  is favored



Two complicating reactions that decrease the yield are



with  $k \sim 5 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$  for reaction 22,<sup>43</sup> and with  $k = 2.5 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$  for reaction 23.<sup>44</sup> The photochemical quantum yield of  $\text{I}_3^-$  formation can attain a maximum value of  $1/2$  on account of reactions 18 and 20 and assuming a triplet yield of unity, but the reverse reactions and reactions 22 and 23 should considerably decrease it. On the other hand, downstream reactions 25–27 increase the overall photochemical quantum yield: Assuming that a superoxide ion is formed, it reacts in turn according to eq 24 but also by dismutation (eq 25)

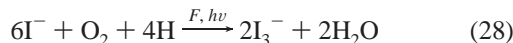


At pH 7.4, nonelementary reaction 25 is relatively slow, with<sup>45</sup>  $k = 2 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$ . Reactions 18 and 21 should account for the dependence of the photochemical yield with the concentration of iodide (Figure 6). For low iodide concentrations, these reactions are slow, and almost no net reaction is observed. If the concentration of iodide is increased, reactions 18 and 21 gradually become more important, and the overall

reaction proceeds to the formation of  $I_3^-$  with increasing efficiency. Going down along the oxygen reduction chain,<sup>45</sup> the final product is water, with further oxidation of two more iodide ions



From the known redox potentials of the relevant pairs,<sup>38,45</sup> it can be concluded that the above reactions are thermodynamically allowed, and they are again favored by a high concentration of iodide. Assuming complete regeneration of the fullerene, the overall chemical reaction is thus



From this equation, from the known concentration of oxygen ( $[O_2] = 3 \times 10^{-4} \text{ mol L}^{-1}$ ), and from the maximum concentration of triiodide attained ( $[I_3^-] = 6 \times 10^{-5} \text{ mol L}^{-1}$ ), it can be concluded that oxygen was not significantly depleted under the experimental conditions, even for the highest recorded times.

The photochemical quantum yield is, among other things, a function of the probability of back-reaction, eq 19. In the absence of dissolved  $O_2$ , the back-reaction 19 cannot in fact be neglected, and the photochemical quantum yield is practically zero. If it is assumed next that back-electron transfer with ground-state fullerene formation is negligible and that oxygen is present, then it is the back-reaction 24 that dictates the quantum yield. If it is overwhelmingly dominant in determining the fate of the superoxide, the reaction cannot proceed, and the quantum yield is again negligible. If, however, reaction 25 is the dominant one, the maximum quantum yield of  $I_3^-$  formation is 1 (2  $I^-$  produced per photon absorbed).

The real quantum yield, in any case, is lower than the respective maximum possible value, owing to reversible steps and to all competing processes not leading to oxidation of  $I^-$ . From Figure 6, a clear linear dependence on  $[I^-]$  is observed, with quantum yields higher than 0.1 for iodide concentrations higher than  $0.2 \text{ mol L}^{-1}$ , and already close to the theoretically maximum value.

From the mechanistic point of view, the present reaction qualifies as a type I photosensitized oxidation,<sup>46</sup> where only ground-state oxygen is involved. In such a case, reaction of the (triplet) sensitizer occurs with the substrate in a first step, and in a second step, the radical anion of the sensitizer is in turn oxidized by  $^3O_2$ , yielding the superoxide ion. Although triplet fullerenes efficiently react with  $^3O_2$  to yield singlet oxygen and  $I^-$  oxidation by singlet oxygen has been reported,<sup>47</sup> a type II photosensitized oxidation,<sup>46</sup> where singlet oxygen formation by reaction of  $^3O_2$  with the (triplet) sensitizer is the first step, can be safely ruled out on the grounds of the relative concentrations of dissolved oxygen and iodide.

## 5. Conclusions

Using steady-state and time-resolved fluorescence, we studied the singlet state properties of a  $C_{60}$  methanoderivative whose addend is a water-soluble dendrimer. The study of fluorescence quenching by halide ions in aqueous solution was carried out at several temperatures. From a new relation for the activation energy of a diffusion-influenced reaction, eq 15, and from a comparison with the fluorescence quenching in organic solvents by neutral halogenated compounds, it is concluded that the quenching in aqueous solution occurs by the external heavy-

atom effect. The existence of an efficient photoinduced oxidation of iodide in aerated solutions and in the presence of the dendro-[60]fullerene is also reported. The photoinduced oxidation is shown to be consistent with a mechanism where only ground-state oxygen is involved.

**Acknowledgment.** This work was supported by the TMR program of the European Union (Research Network Contract ERB FMRX-CT 98-0192 DG12-DLCL) and by the Fundação para a Ciência e a Tecnologia, Portugal (Contract POCTI/34400/QUI/2000).

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