

Monomeric Azaheterofullerene Derivatives $RC_{59}N$: Influence of the R Moiety on Spectroscopic and Photophysical Properties

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Abstract: We have synthesised nine monomeric azaheterofullerene (AZA) derivatives, $RC_{59}N$, with a wide variety of different side chains R and investigated their spectroscopic and photophysical properties in toluene and *o*-dichlorobenzene (ODCB). Measurements include their ground-state absorption spectra, molar absorption coefficient (ϵ_G), fluorescence spectra, fluorescence quantum yields (Φ_F), singlet-state lifetimes (τ_F), triplet-state absorption spectra, triplet molar absorption coefficients (ϵ_T), singlet oxygen

(Φ_Δ), and triplet state (Φ_T) quantum yields. The replacement of a carbon by a nitrogen atom in the C_{60} sphere strongly affects most of the spectroscopic and photophysical properties. The chemical nature of the R moiety has definite effects on these properties in contrast with minor effects on the

chemical nature of the addends in [6,6]-ring bridged monoadduct methano[60]fullerene derivatives. These effects concern properties of the ground state, singlet excited state, and triplet states of our nine $RC_{59}N$ derivatives and in particular the values of photophysical parameters ϵ_G , ϵ_T , Φ_Δ , and Φ_T , which are significantly lower than those of analogous monoadduct [6,6]-ring bridged methano[60]fullerene derivatives.

Keywords: flash photolysis • fullerenes • pulse radiolysis • synthetic methods • triplet-state properties • UV/Vis spectroscopy

Introduction

In heterofullerenes one or more carbon atoms in the C_{60} skeleton are substituted by heteroatoms, leading to an alteration of the electronic and geometric properties of the origi-

nal C_{60} framework. Azaheterofullerenes (AZA), in which one carbon atom in the C_{60} sphere is substituted by nitrogen, a trivalent atom with a lone pair of electrons, are the only class of heterofullerenes that has been isolated in macroscopic quantities.^[1–4] The first isolated AZA was the dimer

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(C₅₉N)₂,^[1] in which the two C₅₉N moieties are linked by an sp³ carbon atom, adjacent to the nitrogen atom embedded in the fullerene framework. The dimer bond is relatively weak (18 kcal mol⁻¹) and can undergo homolysis through photolysis or thermolysis leading to free-radical reactions. The (C₅₉N)₂ synthesis was followed by the preparation of monomeric C₅₉N derivatives such as the hydroazafullerene HC₅₉N.^[2] Replacement of a C₅₉N moiety in the dimer by an R group leads to the formation of RC₅₉N derivatives, in which the R is always bound to the C atom that forms a [6,6] bond with the heteroatom.^[4-6]

The presence of the extra electron on the nitrogen atom in the C₆₀ core results in a modification of molecular orbitals of AZA, RC₅₉N, as compared to their C₆₀ analogues. This alteration leads to a change in the spectroscopic and photophysical properties of these derivatives and particularly their photosensitisation efficiencies, an important feature for potential applications in material science and biology.

In this study, we have synthesised monomeric AZA derivatives, RC₅₉N, bearing different R groups (Figure 1) and determined their spectroscopic and photophysical properties in toluene and *o*-dichlorobenzene. The absorption spectra of the ground state have been determined between 300 and 900 nm. Steady-state and time-resolved fluorescence meas-

urements have been used to characterise the singlet excited state, in particular the quantum yields of fluorescence, Φ_F, the singlet-state lifetimes (τ_F), and the fluorescence spectra. Nanosecond laser flash photolysis and pulse radiolysis have been employed to determine triplet-excited-state properties, including triplet-state absorption spectra, triplet molar absorption coefficients, ε_T, singlet-oxygen, and triplet-state quantum yields, Φ_Δ and Φ_T.

The spectroscopic and photophysical properties of these nine AZA derivatives are compared in this study with those of fullerene C₆₀,^[7] the hydroazafullerene HC₅₉N,^[8,9] the dimer (C₅₉N)₂,^[1] (Ph₂CH)C₅₉N,^[6] the alkoxide ROC₅₉N (with R = O(CH₂)₂OMe) in cyclohexane,^[10] three arylated azafullerenes ArC₅₉N,^[11] the fullerene-heterofullerene dyad C₆₀-C₅₉N,^[4e] and methano[60]fullerene monoadduct derivatives,^[12,13] in particular C₆₀[C(COOEt)₂] here denoted as F.^[14]

Results and Discussion

Ground-state absorption spectra in toluene and *o*-dichlorobenzene: Solutions of azaheterofullerene compounds in toluene and *o*-dichlorobenzene are green-yellow in colour. At

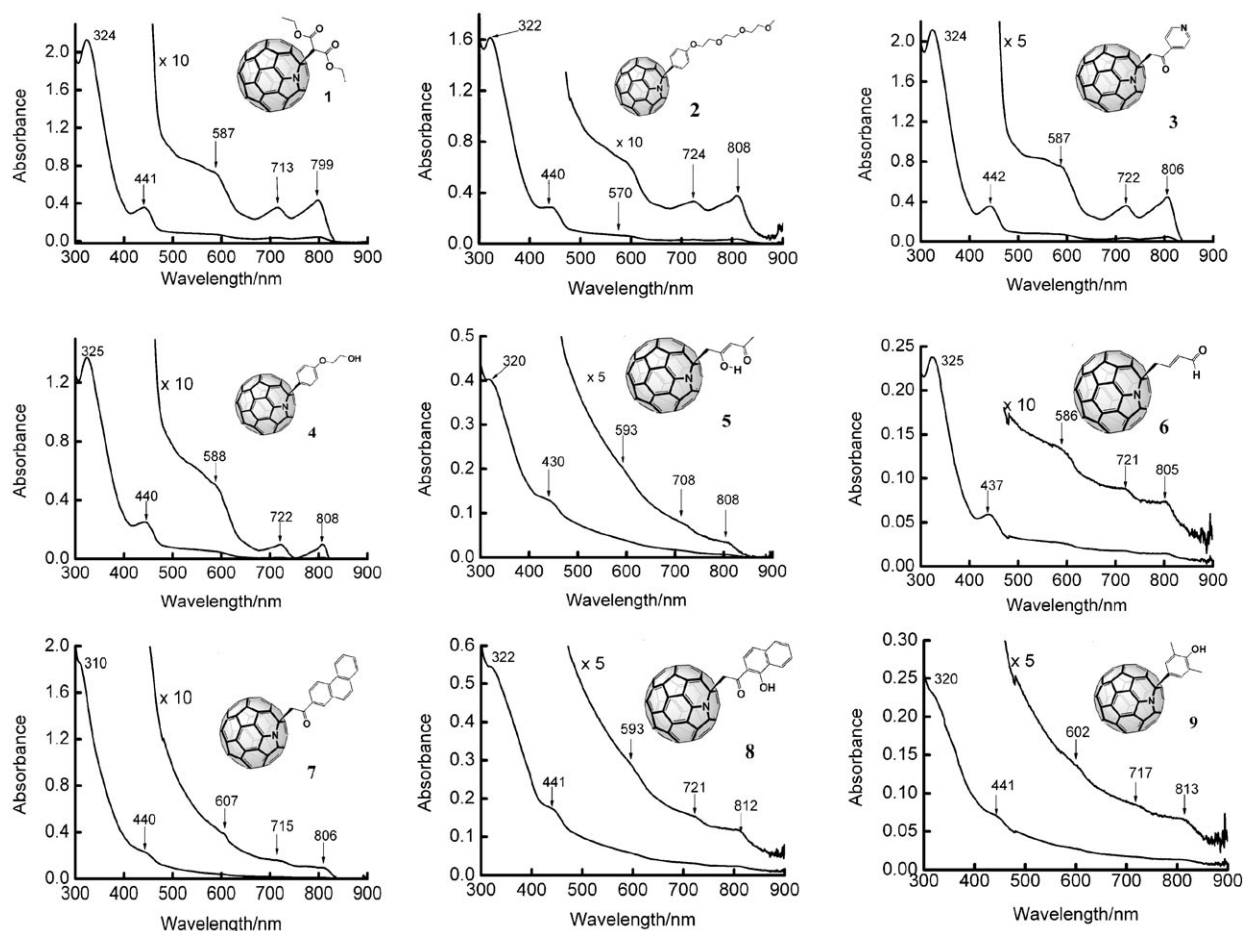


Figure 1. Structure and ground-state absorption of the azaheterofullerenes 1–9 in toluene. Absorbances in arbitrary units.

approximately 10^{-5} M, compounds **1–4** dissolve more easily in both solvents than compounds **5–9**. The ground-state absorption spectrum of each of the nine $RC_{59}N$ derivatives is rather similar in both solvents, with no increase of solubility in *o*-dichlorobenzene. The spectra recorded in toluene are shown in Figure 1. They exhibit bands at 310–325, 430–442, 708–724, and 799–813 nm, with a shoulder at 570–607 nm (Table 1). The absorption bands observed for compounds **1–4** are generally sharper than those observed for compounds **5–9**.

Table 1. Wavelengths [nm] of maxima and shoulders of the ground-state absorption spectra of **1–9** in toluene (Figure 1).

Compound	λ_1	λ_2	$\lambda_{3(\text{sh})}$	λ_4	λ_5
1	324	441	587	713	799
2	322	440	570	724	808
3	324	442	587	713	799
4	325	440	588	722	806
5	320	430	593	708	808
6	325	437	586	721	805
7	310	440	607	715	806
8	322	441	593	721	812
9	320	441	605	717	813

In the ultraviolet region between 300 and 400 nm: Each absorption spectrum of the nine azafullerenes exhibits a band located between 310 and 325 nm ($\epsilon_G \sim (2.8–3.2) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) in toluene that is blue-shifted from the 328 nm peak of the C_{60} absorption in *n*-hexane that corresponds to the allowed $3^1T_{1u} \leftarrow 1^1A_g$ transition of C_{60} ,^[7] the molar absorption coefficient of which is $6.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. The UV band associated with our $RC_{59}N$ derivatives is also related to the 325–329 nm band of the methano[60]fullerene monoadducts in *n*-hexane and cyclohexane.^[12,13] This UV band corresponds to a similar band observed for other AZA derivatives at i) 324 nm for the hydroazafullerene $HC_{59}N$ in toluene,^[2] ii) 320–325 nm in toluene for the dimer $(C_{59}N)_2$,^[1,2] iii) 328 nm for the fullerene–azafullerene dyad in 1,2-dichlorobenzene,^[4e] iv) 321 nm for the alkoxide $ROC_{59}N$ with $R = O(CH_2)_2OMe$ in cyclohexane^[10] and v) 320–323 nm for three monoarylated heterofullerenes $ArC_{59}N$ in cyclohexane.^[11] The set of sharp bands observed for C_{60} between 380 and 410 nm associated with the allowed $1^1T_{1u} \leftarrow 1^1A_g$ transition^[15] are not observed as resolved features in the spectra of the AZA derivatives.

In the visible region between 400 and 620 nm: An absorption band at 434–442 nm with a broad shoulder at 570–607 nm is observed for the nine azaheterofullerenes **1–9** (Table 1). This band and this shoulder are similar to the absorption features observed for i) $HC_{59}N$ (446, 596 nm in toluene),^[2,9] ii) $(C_{59}N)_2$ (446, 596 nm in toluene),^[1,2,10] iii) $(Ph_2CH)C_{59}N$ (446, 596 nm in toluene)^[6] iv) $ROC_{59}N$ (436, 582 nm in cyclohexane),^[10] v) three monoarylated $ArC_{59}N$ (436–44, 580–591 nm in cyclohexane)^[11] and vi) the fullerene–heterofullerene dyad $C_{60}-C_{59}N$ (447, 596 nm in 1,2-dichlorobenzene).^[4e] In the visible region the spectra of **1–9**

differ in important aspects from that of the parent C_{60} . Apart from a band around 440 nm, we note that two sets of broad bands that are prominent in the C_{60} spectra and the principal maxima of which are at 540 and 600 nm,^[7] do not appear as such in the AZA monoadducts.^[1,4e,6,8–11] In the visible region, the spectra of **1–9** do not exhibit the sharp peak at 429–433 nm and the broad band at 490–492 nm that are characteristic of the monoadduct methano[60]fullerenes.^[12,13]

In the red and near-infrared region between 700 and 820 nm: Each absorption spectrum of the nine azafullerenes shows two weak principal bands in this region at 708–724 nm and at 799–813 nm. The interval between these bands is about $1480–1580 \text{ cm}^{-1}$ probably corresponding to a $C=C$ or $C-N$ vibration in the excited state. These two principal bands of our $RC_{59}N$ in the red part of the spectrum are also present in the spectra of other azaheterofullerenes including i) $C_{59}N^+$ at about 1.8 eV (689 nm) and 1.61 eV (770 nm) in toluene,^[16] ii) $HC_{59}N$ (738, 818 nm in *o*-dichlorobenzene, carbon disulfide, and toluene),^[2,9] iii) $(C_{59}N)_2$ (720–738, 800–818 nm in toluene),^[1,2,10] iv) $(Ph_2CH)C_{59}N$ (720–738, 800–818 nm in toluene),^[6] v) $ROC_{59}N$ (710, 789 nm in cyclohexane)^[10] and vi) three monoarylated $ArC_{59}N$ (711–723, 789, 793 nm in cyclohexane).^[11] In the fullerene–heterofullerene dyad $C_{60}-C_{59}N$ in cyclohexane only a band at 726 nm is observed.^[4e]

For **1–9**, the first singlet-excited-state energy (see later) is lower than that of the parent C_{60} and that of the C_{60} monoadduct methano[60]fullerene derivatives, for which the S_0-S_1 absorption bands are observed at 691–698 nm.

Singlet-excited-state properties in toluene: Fluorescence emission spectra of compounds **1–4**, and **7** (Figure 2a) show

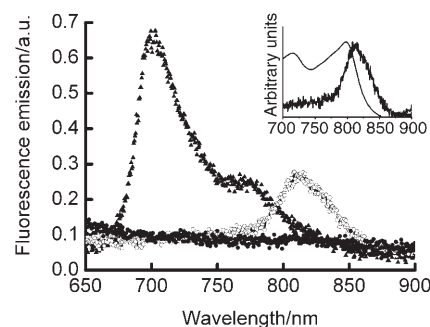


Figure 2. Fluorescence spectra of standard $C_{60}[C(COOEt)_2]$, compound **F** (\blacktriangle), of azafullerene **1** (\circ), and azafullerene **5** (\bullet) in toluene. Inset: normalised absorption and fluorescence spectra of compound **1**. Excitation wavelength: 530 nm, absorbances $A = 0.1$ at 530 nm for all compounds.

wavelength maxima λ_{max} at 812–824 nm (Table 2). These emission spectra are mirror images of the S_0-S_1 absorption bands as shown in the case of **1** (inset Figure 2a). Compounds **2–4** and **7** give emission spectra identical to that of **1** (Figure 2). The AZA emission band is red-shifted by about 110 nm as compared to that of the standard methanofuller-

Table 2. Molar absorption coefficients, ϵ_G at 324 nm, fluorescence lifetimes τ_F , wavelength maxima λ_{\max} of the fluorescence spectra, radiative rate constant $k_r = \Phi_F/\tau_F$ in 10^5 s^{-1} , and energy values, E_S , of the first singlet-excited state S_1 of C_{60} , $C_{60}[\text{C}(\text{COOEt})_2]$ (**F**), and RC_{59}N azafullerenes, in toluene.

Compound	$\epsilon_G(324)$ [$\text{M}^{-1} \text{ cm}^{-1}$]	τ_F [ns]	Φ_F in 10^{-4}	k_r in 10^5 s^{-1}	λ_{\max} [nm]	E_S [kJ mol^{-1}]
C_{60}	62000 ^[a]	1.2 ^[b]	1	0.8	660 ^[b]	193 ^[b]
F ^[c]	–	1.5	4.9	3.3	705	172
1	28000 ± 5600	0.79	2.2	2.8	812	148
2	32000 ± 6400	0.79	2.8	3.5	822	145
3	–	0.77	2.6	3.4	818	146
4	–	0.69	2.1	3.0	821	146
7	–	0.76	3.5	4.6	824	145

[a] From ref. [7]. [b] From ref. [31]. [c] From ref. [28].

ene monoadduct $C_{60}\text{-C}(\text{COOEt})_2$ (that is, **F**). Compounds **5**, **6**, **8** and **9** do not exhibit a measurable fluorescence as typically shown for **5** in Figure 2.

Fluorescence quantum yields, Φ_F , were determined by using Equation (1):

$$\Phi_F = \frac{F_{AZA}}{F_{St}} \times \frac{1 - 10^{-A_{St}}}{1 - 10^{-A_{AZA}}} \times \frac{n_{AZA}^2}{n_{St}^2} \times \Phi_{St} \quad (1)$$

where A is the absorbance of the solution at the excitation wavelength, F is the area of the fluorescence spectrum, and n is the refractive index of the solution. The subscripts AZA and St refer to the studied compound and the standard, respectively. In our measurements, the index of refraction n is similar for both the AZA derivatives and the standard solutions ($n_{AZA}^2 \approx n_{St}^2$), since the absorbances $A = 0.1$ at the excitation wavelength 530 nm and the solvents were identical. By using the methanofullerene monoadduct $C_{60}\text{-C}(\text{COOEt})_2$ as a standard for which $\Phi_F = 4.9 \times 10^{-4}$,^[28] the Φ_{AZA} values of our five compounds (**1–4** and **7**) are between 2.2 and 3.5×10^{-4} in toluene (Table 2). Previously, for **1**, a fluorescence quantum yield, $\Phi_F = 1.6 \times 10^{-4}$, has been reported with no fluorescence standard indicated.^[17] For azafullerenes with R groups different from ours, fluorescence quantum yields with values ranging from $\sim 1.3\text{--}6.4 \times 10^{-4}$ have been reported,^[4f,g,17] with a near-infrared fluorescence emission (λ_{\max} at 825 nm). The fact that **5**, **6**, **8**, and **9** do not exhibit measurable fluorescence indicates that the nature of the addend R can play an important role in the deactivation of the singlet excited state of the RC_{59}N compound.

Fluorescence lifetimes (τ_F) of **1–9**, which were obtained by picosecond laser excitation, ($\tau_F \sim 0.69\text{--}0.79$ ns) are reported in Table 2. These parameters allow a calculation of the radiative rate constants k_r indicated in Table 2. Energy values, E_S , of the first singlet excited state S_1 , calculated from the 0–0 transition considered to be at the intersection of the normalised absorption and fluorescence spectra, are between 145 and 148 kJ mol^{-1} (Table 2). These E_S values are $\sim 25\text{--}28 \text{ kJ mol}^{-1}$ lower than that of monoadduct derivative **F**. The remarkably constant values of E_S , although 50 kJ below that of C_{60} , show that the R moiety hardly affects the

fullerene core when a nitrogen atom is within the fullerene skeleton. We note however that, in the AZA, the nitrogen atom lowers the E_S value more than an external nitrogen containing adduct, for which E_S is similar to that of adduct **F**.^[15]

Triplet excited-state properties

Triplet absorption spectra in toluene: The absorption profiles of the triplet minus singlet ground state difference absorption spectra of **3**, **4** and **7** obtained by laser excitation at 355 nm between 425 and 1000 nm show two maxima located at 650 and 850 nm (Figure 3). An additional band at 500 nm

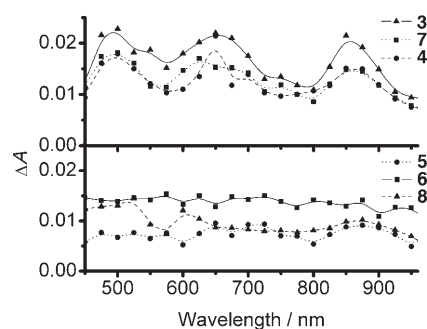


Figure 3. Triplet-minus-singlet difference absorption spectra of azafullerenes **3–8** in toluene recorded 1.5 μs after the laser flash (laser energy: 12 mJ).

is most probably related to the ground-state depletion becoming important below 500 nm. These difference absorption spectra between 450 and 950 nm are similar to those previously reported by Guldi and co-workers who reported a weak band at 1040 nm for compounds **2** and **3** over a spectral range extending more into the red region.^[17] They differ from the T–T spectrum of HC_{59}N that exhibits a very distinct difference absorption spectrum with a main band at 750 nm.^[9] For compounds AZA**5**, AZA**6**, and AZA**8**, although there is definite triplet absorption, no individual bands are observable.

Determination of the quantum yields of singlet oxygen production, Φ_Δ : The quantum yield Φ_Δ of the sensitised photo-production of singlet oxygen ($^1\text{O}_2$, $^1\Delta_g$) by the triplets of **1–9** in toluene was assessed by a comparative method similar to that used for the determination of Φ_T .^[18] We compared the slopes of linear plots of I_0 (the amplitude of the time-resolved $^1\text{O}_2$ ($^1\Delta_g$) 1270 nm phosphorescence signal extrapolated to $t = 0$) versus laser intensity, with the slopes obtained for optically-matched solutions of the standard compound St, C_{60} . The ratio of the slopes, α^{AZA} , of $^1\text{O}_2$ production sensitised by the AZA compound as a function of the laser intensity, to the corresponding slopes, α^{St} , determined for $^1\text{O}_2$ production sensitised by the standard, C_{60} , as a function of the laser intensity, allows the determination of the quantum yield of singlet-oxygen production by the AZA compound

from the slope ratio, (after correction for any small differences in the fraction of light absorbed by the solutions at the laser excitation wavelength, λ_{exc}), through Equation (2):

$$\Phi_{\Delta}^{\text{AZA}} = \Phi_{\Delta}^{\text{St}} \times \frac{\alpha^{\text{AZA}}}{\alpha^{\text{St}}} \times \frac{1 - 10^{-A_{\lambda_{\text{exc}}}^{\text{St}}}}{1 - 10^{-A_{\lambda_{\text{exc}}}^{\text{AZA}}}} \quad (2)$$

where $A_{\lambda_{\text{exc}}}^{\text{St}}$ and $A_{\lambda_{\text{exc}}}^{\text{AZA}}$ are the absorbances for the standard and for the azafullerene solutions at the excitation wavelength, 355 nm with $\varphi_{\Delta}^{\text{St}}$ of the standard, C_{60} , being near unity.^[19] The nine measured Φ_{Δ} values are given in Table 3

Table 3. Quantum yields of singlet-oxygen production Φ_{Δ} in toluene and *o*-dichlorobenzene (ODCB), molar triplet absorption coefficients, ε_{T} at 880 nm, measured by two independent methods in toluene and triplet quantum yields Φ_{T} .

Compound	Φ_{Δ} (toluene)	Φ_{Δ} (ODCB)	$\varepsilon_{\text{T}}(880)^{[\text{d}]}$ [M ⁻¹ cm ⁻¹] (p.r.)	$\Phi_{\text{T}}^{[\text{e}]}$	$\varepsilon_{\text{T}}(880)^{[\text{f}]}$ [M ⁻¹ cm ⁻¹] (l.f.p.)
C ₆₀	1 ^[a]	–	–	1	–
F	0.97 ^[b]	–	–	–	–
C ₅₉ NH	0.48 ^[c]	–	–	–	–
1	0.24	0.24	–	–	–
2	0.22	0.22	–	–	–
3	0.23	0.23	–	–	5200
4	0.24	0.27	4800	0.24	5000
5	0.16	0.14	–	–	–
6	0.16	0.18	–	–	–
7	0.26	0.19	5100	0.26	4100
8	0.25	0.21	–	–	–
9	0.17	0.21	–	–	–

[a] From ref. [19]. [b] From ref. [14]. [c] From ref. [8]. [d] Determined by triplet energy transfer by pulse radiolysis (p.r.) (see text). [e] Determined by using ε_{T} measured by triplet energy transfer through pulse radiolysis. [f] Determined by the comparative method through laser flash photolysis (l.f.p.) (see text).

for two solvents toluene and *o*-dichlorobenzene. For these determinations the same solvent was used for the AZA derivatives and the standard, since the radiative properties of singlet oxygen are dependent on the solvent. The experimental error can be estimated to be $\pm 15\%$. The Φ_{Δ} values obtained (Table 3) are rather similar in both solvents within the experimental error. They are approximately half the Φ_{Δ} value of 0.48 determined by Tagmatarchis and co-workers for HC₅₉N in toluene.^[8]

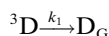
The aggregation of fullerenes can decrease their Φ_{Δ} and Φ_{T} quantum yields.^[13,20] Thus, in order to investigate any dependence of Φ_{Δ} on potential aggregates of **3**, **6** and **8**, Φ_{Δ} was determined for solutions with ground-state absorbances of 0.1 and 0.4–0.5 at the laser excitation wavelength. The Φ_{Δ} values obtained are rather similar for high and low concentrations. This similarity suggests that the relatively low Φ_{Δ} values (0.14–0.26) of RC₅₉N as compared to the near unity values for monoadduct methano[60]fullerenes in organic solvents^[12,13] are not due to aggregation of the AZA derivatives in toluene and *o*-dichlorobenzene.

Determination of the triplet molar absorption coefficients:

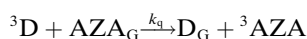
The molar absorption coefficients ε_{T} have been independently determined by pulse radiolysis by using an energy-transfer technique^[21–23] and with laser flash photolysis by using a comparative method.^[18,24,25]

Pulse radiolysis: Pulse radiolysis was used to measure the triplet molar absorption coefficients, ε_{T} , of **4** and **7** in toluene through a method that exploits quantitative triplet-energy transfer. The lowest triplet of each AZA compound in toluene was produced by energy transfer from the triplet excited state of another solute, a donor (D), biphenyl, present in greater concentration (10^{-1} M versus $1\text{--}2 \times 10^{-4}$ M), with a triplet molar absorption coefficient at 365 nm^[22] of $27100 \text{ M}^{-1} \text{ cm}^{-1}$. Three reactions must be taken into account in this system with respective rate constants, k_1 , k_2 , k_3 :

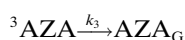
1) Decay of the donor triplet, ^3D , to its ground state, D_G :



2) The energy-transfer reaction from ^3D to AZA_G, the ground state of the AZA:



and 3) Decay of the acceptor triplet ^3AZA to its ground state while it is formed:



with $k_2 = k_1 + k_q[\text{AZA}]$. Values of the rate constants obtained for **4** are $k_1 = 3 \times 10^4 \text{ s}^{-1}$, $k_2 = k_1 + k_q[\text{AZA}] = 1 \times 10^5 \text{ s}^{-1}$, and $k_3 = 7.5 \times 10^4 \text{ s}^{-1}$.

Taking into account a correction due to the decay of the donor triplet (^3D) through routes other than energy transfer and a correction due to a decay of the acceptor triplet (^3AZA) during its formation leads to the molar absorption coefficient of **4** at 880 nm [Eq. (3)]:

$$\varepsilon_{\text{T}}(^3\mathbf{4})_{880} = \varepsilon_{\text{T}}(^3\mathbf{D})_{365} \times \frac{\Delta A_{880}(^3\mathbf{4})}{\Delta A_{365}(^3\mathbf{D})} = 4800 \pm 700 \text{ M}^{-1} \text{ cm}^{-1} \quad (3)$$

where $\Delta A_{880}(\mathbf{4})$ is the corrected value of the maximum transient absorbance of the triplet $^3\mathbf{4}$ at 880 nm and $\Delta A_{365}(^3\mathbf{D})$ is the transient absorbance of the biphenyl donor triplet at 365 nm.

For **7**, a rather similar value was obtained $\varepsilon_{\text{T}}(^3\mathbf{7})_{880} \sim 5100 \pm 800 \text{ M}^{-1} \text{ cm}^{-1}$. In both $\varepsilon_{\text{T}}(\mathbf{4})$ and $\varepsilon_{\text{T}}(\mathbf{7})$ determinations, the molar absorption coefficients of the ground state, $\varepsilon_{\text{G}}(\mathbf{4})$ and $\varepsilon_{\text{G}}(\mathbf{7})$ at 880 nm, are considered as negligible.

By using these molar absorption coefficients we were able to determine the Φ_{T} of **4** and **7** by a comparative method.^[18,24] Linear plots of the absorbance changes extrapolated at $t=0$ and observed at appropriate monitoring wavelengths versus laser intensity were constructed. The

slopes of these linear plots are β^{AZA} for solutions of the AZA derivative and β^{St} for solutions of the standard C_{60} in toluene, for which $\varepsilon_T^{St} = 20200 \text{ M}^{-1} \text{ cm}^{-1}$ at 750 nm^[26] and $\Phi_T^{St} \sim 1$.^[19] The Φ_T^{AZA} of **4** and **7** can be calculated by using the expression (4):

$$\Phi_T^{AZA} = \Phi_T^{St} \times \frac{\Delta A^{AZA}}{\Delta A^{St}} \times \frac{\varepsilon_T^{St}}{\varepsilon_T^{AZA}} \times \frac{1-10^{-A_{St}}}{1-10^{-A_{AZA}}} \quad (4)$$

where A_{St} and A_{AZA} are the absorbances for the standard and for the AZA solutions at the excitation wavelength, 355 nm, with Φ_T^{St} of the standard, C_{60} , being near unity.^[19] The triplet quantum yields Φ_T of **4** (0.24) and **7** (0.26), thus calculated, are very similar to the quantum yields of singlet-oxygen photosensitised production, Φ_Δ , reported in Table 3. The parameters Φ_T and Φ_Δ are related by the product [Eq. (5)]:

$$\Phi_\Delta = \Phi_T S_\Delta S_O \quad (5)$$

where S_Δ is the fraction of triplet states quenched by oxygen leading to formation of singlet oxygen and S_O is the fraction of triplet states quenched by oxygen.^[27]

Thus, for **4** and **7**, it can be concluded that S_Δ and S_O are near unity as already observed for C_{60} and methano[60]fullerene derivatives.^[12] These Φ_T values for **4** and **7** (Table 3) are consistent with the Φ_T value equal to 0.30, previously determined for **1** and for another $RC_{59}N$ compound with $R = \text{phenyl-OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$, by a method that was not stated by the authors.^[17] Previously, relative triplet quantum yields Φ_T have been reported^[4g] for five AZA compounds with substituent R different from ours (except for **7**). These relative Φ_T values were between 0.88 and 0.98, related to an arbitrary value of unity for Φ_T of an AZA compound, 2-azafullerenyl-1-(phenyl)ethanone, chosen as standard, with no corresponding triplet molar absorption coefficients indicated.^[4g]

Laser flash photolysis: For **4** and **7**, we have observed that the quantum yields of singlet oxygen and triplet production, Φ_T and Φ_Δ , are very similar (Table 3) and thus that $S_\Delta = S_O = 1$. Assuming that for all the other AZA compounds, S_Δ and S_O are also near unity, and therefore that $\Phi_T = \Phi_\Delta$, it is possible to estimate the triplet-state molar absorption coefficients of the AZA derivatives by using the comparative method.^[21,24] By using Equation (4), expressing Φ_T^{AZA} , reported above, it is possible to write Equation (6):

$$\varepsilon_T^{AZA} = \varepsilon_T^{St} \times \frac{\Phi_T^{St}}{\Phi_T^{AZA}} \times \frac{\beta^{AZA}}{\beta^{St}} \times \frac{1-10^{-A^{St}}}{1-10^{-A^{AZA}}} \quad (6)$$

Equation (6) allowed us to determine the triplet molar absorption coefficients of three compounds in toluene at 880 nm, $\varepsilon_T^{AZA} = 5200$ for **3**, 5000 for **4**, and $4100 \text{ M}^{-1} \text{ cm}^{-1}$ for **7**, values very similar to those reported above and measured by an independent method,^[21-23] by using pulse radiolysis

and triplet-energy transfer (Table 3). For all these AZA derivatives, ε_G is negligible as compared to ε_T at 880 nm.

Conclusion

The replacement of a carbon atom of the C_{60} framework by a nitrogen atom strongly affects most of the photophysical properties of $RC_{59}N$. The ground-state absorption spectra of **1-9** exhibit bands at 320–325, 430–442, 708–724, and 799–813 nm, and a shoulder at 570–607 nm, this shoulder being less noticeable for compounds **5**, **8** and **9**. The visible region of the ground-state absorption spectrum of the monomeric azafullerenes differs from that of monoadducts of methano-fullerenes that display a sharp peak at 429–432 nm, a broad band peaking at 490–492 nm, and weak structures between 650–700 nm with the strongest feature at 691–698 nm.^[12] Moreover, the chemical nature of the R group has definite effects on some spectroscopic and especially photophysical properties of $RC_{59}N$ in contrast with minor effects on the chemical nature of the addend in most monoadduct methano[60]fullerene derivatives. The effects of the nature of the R group concern features of the ground-state and triplet-state absorption spectra, fluorescence properties, as well as values of the photophysical parameters, ε_G , ε_T , Φ_Δ , and Φ_T , that are significantly lower than those of monoadduct methano[60]fullerene derivatives.

Experimental Section

Synthesis of heterofullerene-fluorophore-conjugates 1-9: ($C_{59}N$)₂ (60 μmol), prepared according to literature procedures,^[1] and p -TosOH were dissolved in o -dichlorobenzene (20 mL). The corresponding amount of the aromatics or enolisable-carbonyl compounds (experimental details given in the references and below) was added to the solution, and the mixture was heated to 150 °C for 15 min while a constant stream of air was passed through the solution. The purification of the heterofullerenes **1-9** was performed by flash chromatography and HPLC, all the products were completely characterised by ¹H and ¹³C NMR spectroscopy, IR spectroscopy, and mass spectrometry (spectroscopic data are given in the references and in the paragraphs below).

Diethyl 2-(hydroazafullerenyl)malonate **1** (30 equiv p -TosOH, 15 equiv diethylmalonate, 49% yield).^[4c]

p -[2-[2-(2-Methoxyethoxy)ethoxy]ethoxy]phenylhydroazafullerene (p -MEEEP-hydroazafullerene) **2** (20 equiv p -TosOH, 40 equiv 1-[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]benzene 82% yield).^[4c]

2-(Hydroazafullerenyl)-1-(4'-pyridinyl)ethanone **3** (30 equiv p -TosOH, 200 equiv 4-acetylpyridine, 24.3% yield).^[4d]

1-(Hydroazafullerenyl)-2,4-pentanedione **5** (40 equiv p -TosOH, 20 equiv acetylacetone, 30.8% yield).^[4c]

4-(Hydroazafullerenyl)croton aldehyde **6** (20 equiv p -TosOH, 15 equiv croton aldehyde, 42.1% yield).^[4c]

2-(Hydroazafullerenyl)-1-(phenanthren-2-yl)ethanone **7** (40 equiv p -TosOH, 20 equiv acetylphenanthrene, 14.2% yield).^[4g]

2-[4-(Hydroazafullerenyl)phenoxy]ethanol (**4**) was obtained by a 10 min reaction of ($C_{59}N$)₂ with p -TosOH (10 equiv) and ethylene glycol phenyl monoether (5 equiv) at 150 °C in 33.0% yield. ¹H NMR ($CS_2/CDCl_3$, 400 MHz): $\delta = 8.75$ (AA'BB', 2H), 7.40 (AA'BB', 2H), 4.31 (m, 2H), 4.15 (t, 1H), 4.08 ppm (m, 2H); ¹³C NMR ($CS_2/CDCl_3$, 100.4 MHz): $\delta = 159.51$ (1C), 154.18 (2C), 148.60 (2C), 147.66 (1C), 147.49 (2C),

147.44 (2C), 147.13 (2C), 146.96 (2C), 146.48 (2C), 146.27 (2C), 146.10 (2C), 145.73 (2C), 145.71 (1C), 145.96 (2C), 144.91 (4C), 144.45 (2C), 144.18 (2C), 143.85 (2C), 143.01 (2C), 142.63 (2C), 141.96 (2C), 141.66 (2C), 141.38 (2C), 141.31 (2C), 140.87 (2C), 140.75 (2C), 139.68 (2C), 137.38 (2C), 133.67 (2C), 132.79 (1C), 128.62 (2C), 123.91 (2C), 115.63 (2C), 82.37 (1C), 69.44 (1C), 61.36 ppm (1C); IR (KBr): $\tilde{\nu}$ = 3410, 3012, 2914, 2866, 2813, 1605, 1532, 1505, 1445, 1420, 1345, 1309, 1281, 1252, 1197, 1177, 1102, 1062, 1000, 946, 900, 843, 823, 796, 772, 720, 670, 659, 643, 568, 578, 555, 522, 482, 468 cm^{-1} ; MS (FAB, NBA): m/z : 860 $[M]^+$, 722 $[C_{59}N]^+$.

2-(Hydroazafullerenyl)-1-(1-hydroxynaphth-2-yl)ethanone (**8**) was prepared from the reaction of 2-acetyl-1-naphthol (10 equiv) and *p*-TosOH (20 equiv) with $(C_{59}N)_2$ in 35.1% yield. $^1\text{H NMR}$ ($CS_2/CDCl_3$, 400 MHz): δ = 8.56 (d, 3J = 8.0 Hz, 2H), 8.22 (d, 3J = 8.0 Hz, 1H), 7.83 (d, 3J = 8.8 Hz, 1H), 7.70 (m, 1H), 7.59 (m, 1H), 7.47 (d, 3J = 8.8 Hz, 1H), 7.19 (s, 1H), 5.55 ppm (s, 2H); $^{13}\text{C NMR}$ ($CS_2/CDCl_3$, 100.4 MHz): δ = 200.15 (1C), 163.48 (1C), 154.91 (2C), 148.28 (2C), 147.60 (1C), 147.35 (2C), 147.16 (2C), 146.92 (2C), 146.82 (2C), 146.38 (2C), 146.31 (2C), 146.02 (2C), 145.74 (2C), 145.61 (1C), 145.50 (2C), 144.90 (2C), 144.75 (2C), 144.17 (2C), 144.14 (2C), 143.80 (2C), 142.90 (2C), 142.59 (2C), 141.89 (2C), 141.57 (2C), 141.25 (2C), 141.03 (2C), 140.86 (2C), 140.78 (2C), 139.48 (2C), 137.41 (2C), 137.38 (1C), 134.46 (2C), 130.46 (1C), 127.31 (1C), 126.08 (1C), 125.24 (1C), 124.78 (2C), 124.67 (1C), 123.83 (1C), 118.85 (1C), 113.07 (1C), 78.63 (1C), 49.56 ppm (1C); IR (KBr): $\tilde{\nu}$ = 3423, 2013, 2936, 2851, 1698, 1609, 1548, 1509, 1459, 1422, 1362, 1318, 1239, 1197, 1172, 1107, 1093, 966, 900, 841, 823, 797, 775, 744, 730, 719, 682, 640, 587, 568, 556, 544, 523, 482, 440 cm^{-1} ; MS (FAB, NBA): m/z : 907 $[M]^+$, 722 $[C_{59}N]^+$.

4-(Hydroazafullerenyl)-2,6-dimethylphenol (**9**) was obtained as a black solid in 27.9% yield from reacting $(C_{59}N)_2$ for 15 min with 2,6-dimethylphenol (5 equiv) and *p*-TosOH (10 equiv) at 150 °C. $^1\text{H NMR}$ ($CS_2/CDCl_3$, 400 MHz): δ = 8.04 (s, 2H), 4.95 (s, 1H), 2.58 ppm (s, 6H); $^{13}\text{C NMR}$ ($CS_2/CDCl_3$, 100.4 MHz): δ = 154.19 (2C), 153.24 (1C), 148.92 (2C), 147.62 (1C), 147.49 (2C), 147.43 (2C), 147.06 (2C), 147.05 (2C), 146.43 (2C), 146.22 (2C), 146.05 (2C), 145.70 (2C), 145.66 (1C), 145.48 (2C), 144.88 (2C), 144.86 (2C), 144.38 (2C), 144.13 (2C), 143.84 (2C), 142.95 (2C), 142.57 (2C), 141.91 (2C), 141.63 (2C), 141.40 (2C), 141.25 (2C), 140.81 (2C), 140.70 (2C), 139.60 (2C), 137.38 (2C), 132.73 (2C), 132.61/132.55 (2C/1C), 127.58 (2C), 124.00 (2C), 82.41 (1C), 16.24 ppm (2C); IR (KBr): $\tilde{\nu}$ = 3415, 3016, 2934, 2852, 1612, 1567, 1530, 1515, 1458, 1433, 1422, 1363, 1318, 1197, 1106, 1080, 966, 900, 841, 823, 797, 744, 720, 684, 640, 588, 568, 555, 523, 482, 440 cm^{-1} ; MS (FAB, NBA): m/z : 844 $[M]^+$, 722 $[C_{59}N]^+$.

Spectroscopic studies: Ground-state absorption spectra, at room temperature in toluene and *o*-dichlorobenzene were recorded in the 300–900 nm range, by using a Uvikon 922 spectrophotometer (Kontron Instruments). Steady-state emission spectra in toluene were recorded by a Varian Cary Eclipse spectrofluorimeter upon excitation at 530 nm. Solution absorbances at the excitation wavelength were optically matched at $A = 0.1$. Fluorescence quantum yields were obtained by comparison of the areas of the fluorescence spectra and by using the methanofullerene monoadduct $C_{60}\text{-C}(\text{COOEt})_2$ as a standard for which $\Phi_f = 4.9 \times 10^{-4}$.^[28] Time-resolved fluorescence measurements were performed upon excitation of the samples at 532 nm with a frequency-doubled picosecond Nd:YAG laser (pulse duration 25 ps, $\sim 300 \mu\text{J cm}^{-2}$; Continuum Instrument). The detection wavelength was selected by interference filters and signals were detected with a microchannel plate photomultiplier tube (R2566U, Hamamatsu) and a 7 GHz digitising oscilloscope (IN7000, Intertechnique).

Triplet-state properties were determined by using laser flash photolysis and pulse radiolysis techniques. In the laser flash photolysis experiments, solutions were excited at 355 nm by using a JK Lasers System 2000 Nd:YAG laser^[29] with typical absorbance of 0.3–0.4 in toluene. The detection system consisted of a water-cooled Xe arc lamp and a pulsing unit, high radiance monochromator, and quartz optics. Optical transmissions at various wavelengths selected with the monochromator (bandwidths 2–20 nm) were observed as a function of time before and after the laser flash by using a Hamamatsu R928 photomultiplier.

The pulse radiolysis experiments were carried out with a 12 MeV Radiation Dynamics Ltd (UK) 3 GHz electron linear accelerator. We used a single-pulse mode with a pulse duration from 0.22 to 2 μs and with a peak current of about 30 mA. The accelerator is normally operated at ten pulses per second but the single-pulse mode is achieved by modifying the pulses to the electron gun.^[30] The detection system consisted of a Xe arc lamp and a pulsing unit, high-radiance Kratos monochromator, and quartz optics. Optical transmissions at various wavelengths selected with the monochromator (bandwidths 10–40 nm) were observed as a function of time before and after the laser flash by using photoelectric detection. The output of the photomultiplier (EMI 9558Q) was displayed on a Tektronix TDS 380 digitising oscilloscope. Data processing was performed on a Dan PC by using software developed in house. The sample cell, constructed in Spectrosil quartz, had an optical path-length of 25 mm.

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- [1] J. C. Hummelen, B. Knight, J. Pavlovich, R. González, F. Wudl, *Science* **1995**, 269, 1554.
- [2] M. Keshavarz-K., R. González, R. G. Hicks, G. Srdanov, T. G. Collins, J. C. Hummelen, C. Bellavia-Lund, J. Pavlovich, F. Wudl, K. Holczler, *Nature* **1996**, 383, 147.
- [3] A. Hirsch, B. Nuber, *Acc. Chem. Res.* **1999**, 32, 795.
- [4] a) B. Nuber, A. Hirsch, *Chem. Commun.* **1998**, 405; b) F. Hauke, A. Hirsch, *Chem. Commun.* **1999**, 2199; c) F. Hauke, A. Hirsch, *Tetrahedron* **2001**, 57, 3697; d) F. Hauke, A. Swartz, D. M. Guldi, A. Hirsch, *J. Mater. Chem.* **2002**, 12, 2088; e) F. Hauke, M. A. Herranz, L. Echegoyen, D. Guldi, A. Hirsch, S. Atalick, *Chem. Commun.* **2004**, 600; f) F. Hauke, S. Atalick, D. M. Guldi, J. Mack, L. T. Scott, A. Hirsch, *Chem. Commun.* **2004**, 766; g) F. Hauke, S. Atalick, D. M. Guldi, A. Hirsch, *Eur. J. Org. Chem.* **2005**, 1741.
- [5] W. Andreoni, A. Curioni, K. Holczler, K. Prassides, M. Keshavarz-K., J.-C. Hummelen, F. Wudl, *J. Am. Chem. Soc.* **1996**, 118, 11 335.
- [6] C. Bellavia-Lund, R. Gonzalez, J. C. Hummelen, R. G. Hicks, A. Sastre, F. Wudl, *J. Am. Chem. Soc.* **1997**, 119, 2946.
- [7] S. Leach, M. Vervloet, A. Despres, E. Breheret, J. P. Hare, T. J. Dennis, H. W. Kroto, R. Taylor, D. R. M. Walton, *Chem. Phys.* **1992**, 160, 451.
- [8] N. Tagmatarchis, H. Shinohara, M. Fujitsuka, O. Ito, *J. Org. Chem.* **2001**, 66, 8026.
- [9] N. Tagmatarchis, H. Shinohara, T. Pichler, M. Krause, H. Kuzmany, *J. Chem. Soc. Perkin Trans. 2* **2000**, 2361.
- [10] B. Nuber, A. Hirsch, *Chem. Commun.* **1996**, 1421.
- [11] B. Nuber, A. Hirsch, *Chem. Commun.* **1998**, 405.
- [12] R. V. Bensasson, E. Bienvenue, C. Fabre, J. M. Janot, E. J. Land, S. Leach, V. Leboulaire, A. Rassat, S. Roux, P. Seta, *Chem. Eur. J.* **1998**, 4, 270.
- [13] A. Quaranta, D. J. McGarvey, E. J. Land, M. Brettreich, S. Burghardt, H. Schönberger, A. Hirsch, N. Gharbi, F. Moussa, S. Leach, H. Götinger, R. V. Bensasson, *Phys. Chem. Chem. Phys.* **2003**, 5, 843.
- [14] R. V. Bensasson, M. N. Berberan-Santos, M. Brettreich, J. Frederiksen, H. Götinger, A. Hirsch, E. J. Land, S. Leach, D. J. McGarvey, H. Schönberger, C. Schröder, *Phys. Chem. Chem. Phys.* **2001**, 3, 4679.

- [15] S. Leach, *Israel J. Chem.* **2004**, *44*, 193.
- [16] K. C. Kim, F. Hauke, A. Hirsch, P. D. W. Boyd, E. Carter, R. S. Armstrong, P. A. Lay, C. A. Reed, *J. Am. Chem. Soc.* **2003**, *125*, 4024.
- [17] D. M. Guldi, F. Hauke, A. Hirsch, *Res. Chem. Intermed.* **2002**, *28*, 817.
- [18] R. V. Bensasson, E. J. Land, T. G. Truscott in *Excited States and Free Radicals in Biology and Medicine - Contributions from Flash Photolysis and Pulse Radiolysis*, Oxford University Press, Oxford, **1993**, p. 80.
- [19] M. Terazima, N. Hirota, H. Shinohara, Y. Saito, *J. Phys. Chem.* **1991**, *95*, 9080.
- [20] J.-M. Janot, E. Bienvenue, P. Seta, R. V. Bensasson, A. C. Tomé, R. F. Enes, J. A. S. Cavaleiro, S. Leach, X. Camps, A. Hirsch, *J. Chem. Soc. Perkin Trans. 2* **2000**, 301.
- [21] R. V. Bensasson, E. J. Land, T. G. Truscott in *Excited States and Free Radicals in Biology and Medicine - Contributions from Flash Photolysis and Pulse Radiolysis*, Oxford University Press, Oxford, **1993**, p. 76.
- [22] R. V. Bensasson, E. J. Land, *Trans. Faraday Soc.* **1971**, *67*, 1904.
- [23] R. V. Bensasson, E. J. Land in *Physical Properties of Excited States: A General Method for Measuring Triplet-Triplet Extinction Coefficients, Singlet-Triplet Intersystem Crossing Efficiencies and Related Parameters, in Photochemical and Photobiological Reviews Vol. 3*, Kendrick Smith Plenum Press, New York, **1978**, p. 163.
- [24] B. Amand, R. V. Bensasson, *Chem. Phys. Lett.* **1975**, *34*, 44.
- [25] R. V. Bensasson, C. R. Goldschmidt, E. J. Land, T. G. Truscott, *Photochem. Photobiol.* **1978**, *28*, 277.
- [26] R. V. Bensasson, T. Hill, C. Lambert, E. J. Land, S. Leach, T. G. Truscott, *Chem. Phys. Lett.* **1993**, *201*, 326.
- [27] K. Heihoff, R. W. Redmond, S. E. Braslavsky, M. Rougée, C. Salet, A. Favre, R. V. Bensasson, *Photochem. Photobiol.* **1990**, *51*, 635.
- [28] I. Texier, M. N. B. Santos, R. Bensasson, H. Schönberger, M. Brettreich, A. Hirsch, C. Crowley, A. Rassat in *Recent Advance in the Chemistry and Physics of Fullerenes and Related Materials* (Ed.: P. V. Kamat), ECS, **2000**, p. 223.
- [29] S. Navaratnam, *Photostability of Drugs & Drug Formulations* (Ed.: H. H. Tonnesen), CRC Press, Boca Raton, **2004**, p. 255.
- [30] D. J. Holder, D. Allan, E. J. Land, S. Navaratnam, *Proceedings of European Particle Accelerator Conference, Paris* **2002**, 2804.
- [31] J. W. Arbogast, A. P. Darmanyan, C. S. Foote, Y. Rubin, F. D. Diederich, M. M. Alvarez, S. J. Anz, R. L. Whetten, *J. Phys. Chem.* **1991**, *95*, 11.

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