An Ultra-Long-Lived Triplet Excited State in Water at Room Temperature: Insights on the Molecular Design of Tridecafullerenes

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Abstract: Suitably engineered molecular systems exhibiting triplet excited states with very long lifetimes are important for high-end applications in nonlinear optics, photocatalysis, or biomedicine. We report the finding of an ultra-long-lived triplet state with a mean lifetime of 93 ms in an aqueous phase at room temperature, measured for a globular tridecafullerene with a highly compact glycodendrimeric structure. A series of three tridecafullerenes bearing different glycodendrons and spacers to the C₆₀ units have been synthesized and characterized. UV/Vis spectra and DLS experiments confirm their aggregation in water. Steady-state and time-resolved fluorescence experiments suggest a different degree of inner solvation of the multi-fullerenes depending on their molecular design. Efficient quenching of the triplet states by O₂, but not by waterborne azide anions has been observed. Molecular modelling reveals dissimilar access of the aqueous phase to the internal structure of the tridecafullerenes, differently shielded by the glycodendrimeric shell.

Introduction

Fullerenes, their multi-adduct derivatives and many other carbon-based nanometric-size related species have been proposed as valuable key nanomaterials in different fields such as optoelectronics, photovoltaics, photocatalysis or biomedicine.\[1] Organization of these materials at the nanoscale may play a significant role in their performance, since the way how the nanomaterial is intra-/intermolecularly assembled can be of paramount importance in phenomena such as energy/electron transfer, supramolecular interactions, solvation, or for the delivery of species, when the processes are considered at small length scales.\[2]

A common strategy for the development of applications based on [60]fullerene is the design of multi-adduct derivatives with appropriate substituents imparting good solubility and intra-/intermolecular interactions for the desired purpose.\[3] Hexakis-adducts of C₆₀ are suitable scaffolds for the construction of giant molecules (e.g. tridecafullerenes or carbon nanotube-fullerene conjugates) with promising applications\[4] whose structural implications and photophysical properties, however, have not been completely unravelled yet.

Sugar residues surrounding the hydrophobic C₆₀ core allow excellent solubility of these derivatives in polar solvents like water. Thus, the 1:2 [60]fullerene-γ-cyclodextrin host-guest complex was shown to preserve the fullerene's ability to photosensitize the production of singlet oxygen (hereafter \(^{1}O₂\)) despite a ca. 50% reduction of the fullerene surface accessible to oxygen from the aqueous phase, owing to the effective shielding by the two cycloextrin moieties.\[5] However, in the case of glycodendro[60]fullerene monoadducts, their amphiphilic behavior can cause self-assembly in water (favoured through π-π interactions between the C₆₀ moieties), leading to formation of well-defined compact micellar supramolecular aggregates.\[6] Mannose-derivated conjugates have been widely applied as recognition elements or labelling agents of biological substrates\[7] as key components of sensors\[8] in fluorescence imaging\[9] and in the photo-dynamic therapy of pathogens\[10] or cancer.\[11]

Herein we report on the synthesis, structural and photophysical characterization in water and molecular modelling of
a series of globular glycodendrimeric tridecafullerenes decorated with mannose sugars as terminal units (11–13, Scheme 1 and Scheme 2). These globular multifullerenes display rather long-lived triplet excited states and, in particular, compound 13 shows an exceptionally long mean triplet lifetime of 93 ms in aqueous phase at room temperature. This experimental finding has no precedents in the previous literature, since this value is in sharp contrast with the other much shorter-lived fullerene derivatives under study in this article. Moreover, the ultra-long-lived triplet excited state of compound 13 measured in this work is also well apart from those triplet lifetimes described for other organic molecules or coordination compounds, in solution at ambient temperature, reported so far.[12]

**Results and Discussion**

**Synthesis and Characterization**

The synthesis of tridecafullerenes 11 and 12 was carried out by following a click-chemistry based synthetic strategy as depicted in Scheme 1. From monoadduct 1, hexakis-adduct 3 was obtained by Bingel-Hirsch cycloaddition of (1,2,3-triazole)-(CH=CH)-malonate,[13] yielding the asymmetric derivative appended with ten alkylene moieties and a chloride group at the focal point. Addition of the carbohydrate azides 4 or 5 by copper-catalyzed azide-alkyne cycloaddition (CuAAC)[14] in DMSO, using CuBr·S(Me)₃ as catalyst,[15] leads to the chloride derivatives 6 and 7 which, after treatment with sodium azide, allow the quantitative preparation of the building blocks 8 and 9 appended with 10 and 30 sugar moieties, respectively. From these azide fullerene hexakis-adducts, tridecafullerenes 11 and 12 can be obtained by CuAAC click chemistry reaction with symmetric alkyne derivative 10.[16] Compounds 11 and 12 are endowed with 120 and 360 mannose units, respectively, and were obtained in 83% and 58% yield after purification by ultrafiltration (Amicon®). The synthesis and characterization of tridecafullerene 13 (Scheme 2) has been reported elsewhere.[17] Characterization of all new compounds and their aggregation in water (Figure S1) was carried out by using standard techniques (Supporting Information).

**Photophysical Characterization**

The absorption spectra of tridecafullerenes 11–13 and their hexakis-adduct structural precursors 6 and 7 in PBS solution are depicted in Figure 1 and S2. The UV/Vis spectral features are collected in Table 1 and are in good agreement with previous reports of hexakis-adducts with relatively similar substitution patterns.[17]

A remarkable hypochromic shift was observed in the UV/Vis absorption spectra of tridecafullerenes 11–13 when the absorption coefficients of the peaks in the 269–273 nm region were compared with those of their respective hexakis-adduct precursors × 13 (Figure 1 insert).[18] Hypochromicities were in the 10–15% range for 11 vs. 6 and 12 vs. 7, respectively, while a 30% hypochromic shift was observed in the case of 13 vs. 6. Such a hypochromic effect could be related to solvent exclusion in the case of tridecafullerenes, due to their more compact structure vs. the hexakis-adduct precursors, favouring hydrophobic interactions in the inner domain, and to their tendency to self-aggregate via supramolecular interactions by

| Compound | C₆₀ units | Spacers | Sugars | UV/Vis absorption λₐbs, nm [mm] [c] (ε [mol⁻¹ dm³ cm⁻¹]) |
|----------|-----------|---------|--------|------------------------------------------------------|
| 6        | 0         | 1       | A      | 10 214 (10 7500), 241 sh (68 4000), 269 (52 0000), 276 sh (50 6000), 313 sh (32 1000), 335 sh (23 6000) |
| 11       | 1         | 12      | I A    | 120 213 (10 84600), 247 sh (67 24000), 269 sh (60 39000), 330 sh (32 2600) |
| 7        | 0         | 1       | B      | 30 211 sh (34 9200), 245 (11 0600), 280 (78 800), 309 sh (55 1000), 320 sh (51 300), 332 sh (44 1000) |
| 12       | 1         | 12      | I B    | 360 243 (11 19000), 273 (85 90000), 316 sh (53 94000), 332 sh (45 3300) |
| 13       | 1         | 12      | II A   | 120 244 sh (52 9200), 272 (46 37000), 309 sh (34 18000), 321 sh (30 87000), 331 sh (28 38000) |

[a] The structural features are defined according to the number of [60] fullerene hexakis-adduct units (at the core and/or shell), only shell units are considered in the case of the synthetic precursors 6 and 7, on the type of spacer units between the core–shell fullerenes and the shell fullerene-terminal sugar (mannose), and on the number of terminal sugars at the distal ends of the shell fullerenes, according to Schemes 1 and 2, as follows: core fullerene 10, shell fullerenes 6 or 7, spacer I = CH₂-(CH=CH₂)₉-CH₂-O-(CH₂)₉- spacer II = (CH₂)₉-; spacer A = (CH₂)=O-(1,3,4-triazole)-(1,3,4-triazole)-O-mannose (α); spacer B = (CH₂)₁₀(1,2,3-triazole)-(1,3,4-triazole)-(CH₂)-O-(CH₂)₉-O-(1,3,4-triazole)-(1,3,4-triazole)-O-mannose (α), [b] PBS aqueous solution, pH 7.4. Wavelength uncertainty ± 3 nm for peaks, ± 5 nm for shoulders (sh). [c] Uncertainty ± 15%.

Figure 1. UV/Vis absorption spectra (phosphate saline buffer, PBS solution, pH 7.4) of the mannose-labelled tridecafullerenes 11–13 under study and their corresponding hexakis-adduct structural precursors 6 and 7.
Scheme 1. Synthesis of tridecafullerenes 11 and 12.
hydrogen bonding between the external sugar residues (Figure S1). To some extent, this hypochromism would be similar to the changes in optical density observed when nucleobase interactions are modified in nucleic acids, due to changes in solvent composition or during melting/annealing processes.[19]

Table 2 collects the wavelengths of the fluorescence emission maxima (λ_{em}max) and the lifetimes of the singlet (τ_S) and triplet (τ_T) excited states of tridecafullerenes 11–13 and their corresponding hexakis-adduct structural precursors, 6 for 11 and 13, and 7 for 12. Table 2 also collects the dynamic bimolecular quenching rate constant of the lowest triplet excited states (τ_T) by O₂ (k_{T_S}O₂), the probability of T₁ quenching by molecular oxygen (P₅O₂), and the singlet oxygen production quantum yield (Φ₅) in PBS solution.

A blue shift about 15 nm between λ_{em}max of 6 and 7 is observed (compare spacer A for 6 vs. spacer B for 7 with a larger glycodendrimeric structure and number of sugar units). Tridecafullerenes 11–13 also show blue-shifted emission with respect to their respective monofullerene precursors 6 and 7 (Figure S3). In particular, compound 13 shows a 134 nm shift with respect to 6. These results agree with the hypothesis of decreased solvation illustrated by the hypochromic shift of absorption spectra of tridecafullerenes, especially 13, evidencing a poorer stabilization of the excited singlet state due to less water solvation in the tridecafullerenes.

Moreover, the nanoheterogeneous behavior of these systems is supported by the bi-exponential functions usually required to fit the fluorescence decays (Figure S4). Furthermore, the mean emission lifetimes (τ_{em}) are shorter in 11–13 than in 6 and 7, showing that S₁ is less stabilized in the case of the tridecafullerenes due to reduced interactions with the polar solvent, as confirmed by the higher energy gap of 11–13. Compound 13 shows again an extreme behavior, displaying the shortest fluorescence lifetime (0.22 ns) and highest energy gap.

Concerning the T₂ lifetime in the absence of quenchers (τ_{0,T₂}), longer lifetimes are shown by tridecafullerenes 11–13 in comparison with 6 and 7 (both displaying lifetimes around 60 μs). Almost a twofold increase from 64 to 110 μs can be observed when 11 and 12 are compared (cf. spacer A vs. spacer B with a larger glycodendrimeric structure, Table 1, Scheme 1 and Scheme 2). Furthermore, in the case of compound 13, an extraordinarily long triplet mean lifetime (τ_{em}) of 93 ms was detected, whose discrete components τ₁ and τ₂ are 30 ms (42% amplitude) and 280 ms (58% amplitude), respectively (Table 2, Figure 2 and S5).

According to previous literature reports on the photophysics of [60]fullerene-sugar conjugates (Bingel-type monoadducts), these derivatives show shorter T₂ lifetimes on going from hydrophobic to polar environments (ca. 50 μs in toluene vs. 35 μs in acetonitrile).[22] providing additional support to the hypothesis suggesting lower polarity around the C₆H₆ units of the globular tridecafullerenes vs. the more open monofullerenic hexakis-adduct precursors 6 and 7, due to limited solvent accessibility to the inner domains of 11–13. Moreover, when

![Scheme 2. Structure of tridecafullerene 13.](image)

### Table 2: Photophysical parameters of the mannose-labelled tridecafullerenes 11–13 under study and their corresponding hexakis-adduct structural precursors 6 and 7.

| Compound | λ_{em}max [nm][a] | τ₁ [ns] (% amplitude)[b] | τ₂ [ns] | τ_{em} [μs][c] | τ₁ [μs][d] | k_{i}O₂ [M⁻¹s⁻¹][e] | p_iO₂ def | Φ₅ [f] | τ₂ [μs][f] |
|----------|-----------------|-----------------|-------|---------------|---------|-------------------|----------|-------|---------|
| 6        | 652             | 1.0 (77)        | 3.1 (23) | 1.5           | 50      | 2.7               | 1.30×10^3| 0.95  | 0.11   | 66.2    |
| 11       | 590             | 0.5 (74)        | 2.7 (26) | 1.1           | 64      | 4.2               | 0.82×10^3| 0.93  | 0.02   | 63.5    |
| 7        | 635             | 1.1 (84)        | 4.1 (16) | 1.6           | 53      | 4.4               | 0.77×10^3| 0.92  | 0.13   | 63.0    |
| 12       | 616             | 0.5 (66)        | 3.0 (34) | 1.3           | 110     | 9.1               | 0.37×10^3| 0.92  | 0.05   | 64.6    |
| 13       | 518             | 0.2 (97)        | 2.5 (3)  | 0.22          | 30 000 | 0.42              | 8.50×10^3| 0.99  | 0.07   | 3.2    |

[a] PBS aqueous solution, pH 7.4. [b] Wavelength uncertainty ±10 nm. [c] Singlet excited state lifetime, biexponential fitting of the time-dependent fluorescence intensity decay profiles was usually required (i(t) = A + B × e⁻^[τ₁/τ₂]), where B is the corresponding preexponential factor related to signal amplitude and τ₁ is the discrete lifetime component. Uncertainty ±10%. [d] Triplet excited state lifetime in the absence of quencher. Air-purged deuterated PBS solution. Uncertainty ±10%. [e] Triplet excited state lifetime in the presence of O₂ quencher. Air-equilibrated d-PBS solution. Uncertainty ±10%. [f] Dynamic bimolecular quenching rate constant of triplet excited states by O₂. Uncertainty ±15%. [g] Probability of triplet excited state quenching by O₂ under air-equilibrated conditions. p_iO₂ = 1 - (τ₁/τ₂). [h] Singlet oxygen production quantum yield. Uncertainty ±10%. [i] Singlet oxygen phosphorescence lifetime measured in d-PBS solution with an optical density ≤0.1 at 355 nm (dye concentrations in the 10⁻⁸–10⁻⁶ M range) in very good agreement with the expected Oₛ lifetime in deuterium oxide, 64.4 μs. Uncertainty ±3%. [j] τ₀,T₂ is the preexponential weighted mean lifetime (τ₀,T₂ = ΣB × τ₂/ΣB), where τ₀ and τ₂ stand for the mean lifetime of the singlet and triplet excited states, respectively. Uncertainty ±10%. [k] Biexponential fitting of the triplet excited state decay profile was required. [l] Singlet oxygen lifetime in PBS solution.
the series 11–13 is considered, tridecafullerene 13 is the one showing the longest triplet lifetime (93 ms) and the highest hypochromic shift in the UV/Vis absorption spectrum. It also shows the largest blue-shifted fluorescence and shortest lived $S_1$. These differences in the photophysical properties of 13 may be attributed to the fact that compound 13 has got spacer II (hydrophobic shorter alkyl) vs. I (hydrophilic longer polyether) when 13 and 11, with the same A spacer and number of sugar units, are compared.

It has to be noted that such a long triplet lifetime has never been described for a fullerene derivative at room temperature in the liquid phase. In this way, a triplet lifetime of 0.25 ms for pristine C$_{60}$ in benzene-like solvents has been reported, while lifetimes in the 0.4–55 ms range have only been reported for C$_{60}$ in the solid phase (either for crystalline C$_{60}$ or in glass or rare gas matrices at 1–10 K, 0.4 ms; or in C$_{60}$ thin films, 55 ms) and lifetimes below 0.30 ms have been described for multi-adducts of fullerenes for organic solar cells. Concerning [60]fullerene hexaadducts, phosphorescence lifetimes of 4.4 and 3.7 s have singularly been reported for two hexapyrrolidine derivatives of C$_{60}$ with $T_5$ and $D_5$ symmetry, respectively, at 77 K, again in a glass matrix. In fact, to the best of our knowledge, such an exceptionally long-lived triplet state has never been described in the previous literature on photophysics of organic molecules or coordination compounds in solution at room temperature. Long $T_1$ lifetimes are of particular interest in applications like photocatalysis, photovoltaics, biomedicine and optoelectronics based on nonlinear phenomena.

Concerning quenching by molecular oxygen, the $T_1$ lifetimes of the air-equilibrated aqueous solutions ($\tau_{\text{air}}$) are in the 0.4–9.1 $\mu$s range (cf. 0.29 $\mu$s for C$_{60}$ in toluene), and allowed the determination of the dynamic bimolecular quenching rate constants by O$_2$ ($k_{T_1}^O_2$, Table 2) via Stern-Volmer analysis (Supporting Information). The observed $k_{T_1}^O_2$ are ca. one order of magnitude below the theoretical diffusion control limit in water at 25°C ($\text{Smoluchowski’s theory, } k_{T_1}\text{diff} \approx 7.4 \times 10^8 \text{ M}^{-1} \text{s}^{-1}$), except for 13 (with spacer II vs. 1), and are higher for the series 11 vs. 12 and 6 vs. 7 when spacer A vs. B is concerned and the precursor hexakis-adducts or their corresponding tridecafullerenes are also compared, revealing the consequences of the molecular design. In this way, tridecafullerene 12, the only one with three-branched terminal sugar units (Scheme 1), which should show the most entangled sugar shell, as described in the Computational Analysis section, is the tridecafullerene with the lowest bimolecular quenching constant by dioxygen (0.37 $\times$ 10$^8$ $\text{M}^{-1} \text{s}^{-1}$). This trend is also followed by compound 7, its structural precursor (0.77 $\times$ 10$^8$ $\text{M}^{-1} \text{s}^{-1}$, Table 2) thus revealing a higher steric hindrance towards O$_2$ diffusion. Conversely, and once again, the behavior of compound 13 is specific, since the bimolecular quenching rate constant by O$_2$ (8.5 $\times$ 10$^8$ $\text{M}^{-1} \text{s}^{-1}$) is purely diffusion-controlled given the excellent agreement, within experimental error ($\pm$ 15%), with the theoretical $k_{T_1}\text{diff}^2$ rate constant.

Regarding the probability of $T_1$ quenching by O$_2$ ($P^T_1$), rather high values (> 92%, Table 2) have been observed in all cases under air-equilibrated conditions, according to the long lifetimes of the triplet states providing enough time for the quencher-quenchee encounter to occur. Indeed, compound 13 deserves a special comment again, since its unprecedented long $\tau_{T_1}$ allows for the quantitative quenching of its $T_1$ state by O$_2$.

A study of the O$_2$ production quantum yield ($\Phi_2$) by these compounds sheds light on the efficiency of the intersystem crossing process generating $T_1$, since $\Phi_2$ is limited by the value of the triplet state quantum yield ($\Phi_D$, $\Phi_A$ $\leq$ $\Phi_D$). The $\Phi_D$ values of the hexakis-adducts 6 and 7 (0.11 and 0.13, respectively) are, within experimental error, in excellent agreement with the $\Phi_A$ and $\Phi_D$ values that can be expected for Bingel-Hirsch-type hexakis-adducts (0.11 for $\Phi_D$). On the other hand, the $\Phi_D$ values of tridecafullerenes 11–13 are well below the 0.11 limit of $\Phi_D$ for the hexakis-adduct building block, and show strong differences between them (Table 2). This could also be explained by a different solvent access to the tridecafullerene’s core, consequently influencing, via changes in the polarity around the fullerene units, the $\Phi_D$ value, the stability of $T_1$, and its $\tau_{T_1}$. Indeed, several properties of tridecafullerenes 11–13 such as the UV/Vis hypochromic effect, the presence of aggregates (Figure S1), the blue-shifted emission and shorter fluorescence lifetimes, the increase of $\tau_{T_1}$ from 6, 7 to 11–13 and, moreover, the dependency of the $\Phi_D$ of C$_{60}$ with the polarity of the medium (0.80 in long-chain alkanes vs. 1.0 in benzene), point to a solvent effect influencing $\Phi_D$ of the tridecafullerenes. Therefore, water exclusion from 11–13, by comparison with their hexakis-adduct precursors 6 and 7, seems to be of paramount importance concerning the properties of tridecafullerenes (see also the Computational Analysis section).

In order to gain deeper insight into the role played by the aqueous solvent and its possible exclusion from the inner domains of the tridecafullerenes, the ability of sodium azide to quench the $T_1$ of 13 was examined in deuterated PBS. Compound 13 is ideal for this experiment because its ultralong $T_1$ lifetime provides the highest sensitivity for probing its own microenvironment. On the other hand, azide anion (N$_3^-$) is able to deactivate triplet excited states efficiently through...
energy/electron transfer processes. However, unlike molecular oxygen, the azide anion must be transported by the solvent to the close environment of the excited state in order to deactivate it. Therefore, quenching of $T_1$ of 13 by $N_3^-$ should be dependent on the access of water, as a carrier of azide anions, to the $C_{60}$ units inside the globular structure of the tridecafullerene.

Stern–Volmer analysis of quenching experiments of $T_1$ of 13 by azide yielded a dynamic bimolecular quenching rate constant ($k_{q, \text{azide}}$) of $2.5(\pm 0.5) \times 10^{4}$ M$^{-1}$ s$^{-1}$ (Figure S6), well below the diffusion control limit expected in water ($k_{\text{diff}}$). Furthermore, the decay traces of $T_1$ of 13 show a noticeable decrease of the signal amplitudes at zero time as the quencher concentration increases (Figure S6). This result could be explained if a fraction of those $T_1$ states of 13 reached by $N_3^-$ could be statically quenched. Accordingly, a value of $1.1(\pm 0.3) \times 10^{4}$ M$^{-1}$ was found for the equilibrium constant for complex formation between 13 and sodium azide (Figure S6).

Recently, weak binding interactions between NaN$_3$ and $C_{60}$ have been evidenced by $^{14}$N NMR experiments. In this regard, formation of a yellow complex between $N_3^-$ and 13 has been detected by UV/Vis spectroscopy (Figure 3).

Benesi–Hilbrend plot revealed a deviation of linearity at high concentrations of $N_3^-$ (not shown), suggesting that a second azide ion binds to the initial complex. Indeed, the optical density difference ($\Delta \text{O.D.} = \text{O.D.(13 + N$_3^-$)} - \text{O.D. (13)}$) (Figure S7) shows a maximum that shifts to longer wavelengths with increasing $N_3^-$ concentrations, suggesting the formation of two complexes. The data could be fitted satisfactorily (Figure 3) with a model where a 1:1 complex is initially formed, which binds a second azide ion at higher concentrations. The fit yielded the 1:1 and 1:2 complex formation constants of 741 M$^{-1}$ and 2.2 M$^{-1}$, respectively. The much lower value of the second constant is consistent with the hindrance of a second $N_3^-$ incorporation by the higher electrostatic barrier around the fullerene.

**Computational Analysis**

Theoretical calculations in simplified model systems were performed in order to describe the most characteristic structural features of these glycodendrimeric multifullerenes. Due to the high complexity of 11–13, we started our study with the central (core) [60]fullerene (Supporting Information, Table S1 and Figure S8) and then increased the complexity step by step to the peripheral fullerenes and from the peripheral fullerenes to the final tridecafullerene (see the SI and Figures S9–S12 for more details).

The models made by three $C_{60}$ fullerenes show that the longer the $C_{60}$-$C_{60}$ spacer, I vs. II, the higher the distance between the peripheral fullerenes ($d_1$) and the higher the $\alpha$ angle. In general, isosceles triangle dispositions are reproduced, i.e., the pairs of values for the $d_1$ distance and the $\beta$ angle are very similar (Figure 4, S9 and Table 3).

When the models are functionalized with the external carbohydrates we observe that there is a non-negligible interaction between the peripheral fullerenes because the distances between them ($d_1$) decrease with respect to non-functionalized systems ($M_I$ and $M_{II}$). This fact is corroborated by the interaction energies calculated considering only the two peripheral fullerenes (what we call „Two $C_{60}$” model in Table 3), where the space to the core fullerene was removed. In the two $C_{60}$ model, the structures for $M_{IA}$, $M_{IB}$ and $M_{II}$ were re-optimized, but the variation in the $d_1$ distance is hardly changed with respect to those obtained in the anchored three $C_{60}$ model. The computed interaction energies are significantly different from zero, with values ranging between...
The strength of the interaction depends directly on the distance between fullerenes and the number of interactions between them. Model $M_{IB}$ shows same peripheral $d_1$ distance as non-functionalized fullerene $M_{I}$, however the interaction energy is around $-90 \text{ kcal mol}^{-1}$. Therefore, the length of the $C_{60}$-sugar spacer along with the presence of the three terminal saccharides allows the peripheral fullerenes to interact rather efficiently. The interaction takes place essentially through the hydrogen bonds established between hydroxyl groups of the sugars and the nitrogen atoms of the triazole ring (Figure 5). Somehow, these different interaction energy values define the compactness degree of the glycofullerene, making it more rigid or flexible depending on the strength of the interaction between fullerenes.\cite{32}

To explore the interaction between pairs of fullerenes, some models with five $C_{60}$ containing perpendicular pairs of peripheral fullerenes were also analysed (Figure S12). The results are analogous to those presented before. Interaction between fullerenes within the same pair, i.e., attached to the same cyclopropane ring, compression of structures and isosceles triangle disposition of fullerenes are reproduced.

Furthermore, we find that the interaction between axial and equatorial pairs of fullerenes is somewhat attractive ($\approx -24 \text{ kcal mol}^{-1}$) for the model containing spacers II and A. If a larger $C_{60}$-$C_{60}$ spacer is used, the interaction between two neighbouring adducts is essentially null. This means that shorter spacers induce a more compact globular glycofullerene because the pair of fullerenes are connected, i.e., able to interact, and they are not free as in the case of longer spacers (Figure S12).

In order to have a clearer visualization of the glycodendrimeric tridecafullerene, we constructed from the $M_{IIA}$ model a complete structure for glycofullerene $13$, and then...

### Table 3: Geometrical parameters and interaction energies for models made by three and two $C_{60}$ fullerenes.

| Model$^\text{[a]}$ | Spacers | Compound | Three $C_{60}$ model | Two $C_{60}$ model$^\text{[f]}$ |
|---------------------|----------|----------|-----------------------|-------------------------------|
|                     | $C_{60}$$-$$C_{60}$ | $C_{60}$$-$$sugar$ | $d_1$ [Å] | $d_2$ [Å] | $\alpha$ [°] | $\beta$ [°] | $E$ (PM6)$^\text{[e]}$ | $E$ (DFT)$^\text{[f]}$ |
| $M_I$               | I        | CH$_3$   | 31.3 | 38.5 | 38.6 | 47.9 | 66.1 | 65.9 | 31.3 | 0.0 | 0.0 |
| $M_{II}$            | I        | A        | 11 (52.0 Å)$^\text{[b]}$ | 27.8 | 34.8 | 34.2 | 47.5 | 65.1 | 67.3 | 27.8 | -39.8 | -59.8 |
| $M_{IB}$            | I        | B        | 12 (71.1 Å)$^\text{[b]}$ | 31.1 | 35.9 | 35.9 | 47.0 | 64.3 | 64.4 | 31.1 | -94.5 | - |
| $M_{II}$            | II       | CH$_3$   | 17.4 | 27.5 | 27.8 | 36.8 | 70.7 | 72.5 | 17.4 | 0.0 | 0.0 |
| $M_{IIA}$           | II       | A        | 13 (42.3 Å)$^\text{[b]}$ | 15.7 | 25.5 | 26.6 | 35.0 | 68.9 | 76.1 | 14.5 | -71.8 | -115.0 |

[a] Model systems are defined considering spacers as defined in Table 1 (see also the SI). $M_{II}$, $M_{II}$ and $M_{IIA}$ contain the actual peripheral shells for compounds $11$, $12$ and $13$ and model systems for the core fullerene as shown in Figures S10–S12. $d_1$, $d_2$, $\alpha$ and $\beta$ parameters are defined in Figures 4 (caption) and S9. [b] $M_I$ and $M_{II}$ are the simplest models in which all the malonates are replaced by methylene units, except the ones that link the peripheral and core fullerenes. [c] Estimated radius for the corresponding theoretical model. [d] The two $C_{60}$ models are built from the three $C_{60}$ models by removing the linkers to the core fullerene. [e] Interaction energies at PM6 in kcal mol$^{-1}$ correspond to $E$(two $C_{60}$ model)$-2E(C_{60})$, where the two $C_{60}$ model structures are reoptimized except for $M_I$ and $M_{II}$ entries. [f] All DFT energies were computed from PM6 geometries.

$-40$ and $-115 \text{ kcal mol}^{-1}$ (Table 3).
it was partially relaxed. Figure 6 shows a 3D representation of the computed structure. Compound 13 is presumably quite fluxional given the composition and total number of atoms (7086), but the structure in Figure 6 clearly shows the compactness of this giant molecule, and the presence of interactions between pairs of neighboring fullerenes. It is also relevant to emphasize the pseudo-spherical layer that the sugars make up around the 12 peripheral C_{60}. Probably, this layer is the only part of the molecule that is in contact with the solvent in aqueous solution, while its inside is supposed to have a hydrophobic nature according to the results of the photophysical characterization.

Conclusion

The synthesis and photophysical behavior of a series of tridecafullerenes (a [60]fullerene core surrounded by a shell of twelve C_{60} units endowed with 120 or 360 mannoses and with different linkers) is reported. Triplet excited-state lifetimes of the tridecafullerenes in aqueous solution are strongly dependent on the type of linker between the fullerenes, and short alkyl chains afford structures with longer triplet lifetimes than those with larger polyether-like spacers. Moreover, triplet-state quenching experiments with O_{3} and N_{3} anion suggest limited access of water molecules to the inner
domains of the tridecafullerenes, due to the interweaved chains with terminal sugars (H-bonding network) and the tightness provided, in particular, by the short alkytype spacers connecting the shell fullerenes to the central core unit. Consequently, the intersystem crossing efficiency and the triplet excited-state lifetimes (showing an unprecedented value as long as 93000 µs in the liquid phase at room temperature!) of the tridecafullerenes are modulated. Molecular modelling helps to ascertain the origin of the differences in the experimental photophysical properties of the giant superfullerenes in terms of the dissimilar structural compactness provided by sugars’ shell and the highly hydrophobic nature of the short alkyl spacers among the core–shell C₄₀ units.

The results now reported allow a better understanding of the structure and features of these singular systems, and pave the way to a fine control on the structural, biological and photophysical properties on these less-known but amazing globular-shape multivalent fullerenes. In particular, thanks to the ultra-long triplet lifetime exhibited by one of our tridecafullerenes and the quantitative quenching of this triplet by O₂, the complete trapping of the triplet state by oxygen, even in hypoxic environments, might find applications for the photodynamic treatment of hypoxic tumours. Further work is underway on the exploitation of compounds with ultra-long excited-state triplet lifetimes such as 13 in biomedicine, photovoltaics, photocatalysis, photon upconversion and other nonlinear phenomena like reverse saturable absorption under low irradiance.

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Conflict of interest

The authors declare no conflict of interest.

Stichwörter: fullerenes · glycoconjugates · photochemistry · triplet lifetime · triplet quenching
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