Synthesis and Spectral Characterization of Water-Soluble Derivatives of C$_{70}$ and High-Order Fullerene Mixture (C$_{76}$, C$_{78}$ and C$_{84}$) Achieved by Chemically Induced Air Oxidation

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The direct air oxidation of chemically reduced high-order fullerene carbon structures affords quantitative yields of oxygenated, pH-sensitive water-soluble derivatives of C$_{70}$ and a high-order fullerene mixture (C$_{76}$, C$_{78}$ and C$_{84}$). Reactant fullerenes have been investigated spectroscopically by solution and cross polarization - magic angle spinning (CP-MAS) solid-state $^{13}$C nuclear magnetic resonance (NMR), vibrational Fourier transformed - infrared (FT-IR) and Raman spectroscopy, ultraviolet - visible (UV-VIS) and solid-state near infrared spectroscopy (NIR), X-ray powder diffraction (XRPD), scanning electron microscopy - energy dispersive X-ray spectroscopy (SEM-EDX) and matrix assisted laser desorption ionization - time of flight mass spectrometry (MALDI-TOF MS) techniques. Hydroxylic, ketonic and carboxylic oxygen moieties covalently attached to cluster carbon cages, after the synthesis of such carbon structures. The high reactivity displayed by these carbon clusters indicates that both the molecular convexity and the structural strain are important parameters that easily favour the oxidation of chemically reduced π-delocalised carbon frameworks.

1. Introduction

The employment in biochemistry of fullerene derivatives has received keen attention due to the achievement of a few successfully documented results in multiple relevant biological tasks.$^{(1–6)}$ Among fullerene carbon frameworks, buckminsterfullerene C$_{60}$ has been granted the greatest attention.$^{(7–11)}$ However, a few promising reports indicate that upper fullerene carbon clusters are valuable biochemical molecular tools in several applications.$^{(12–18)}$
Therefore, developing simple methods of water solubilisation for such structures is a great challenge. Alongside with recent fullerene complexation with suitable hydrophilic hosts and usage of specifically designed polar appendages the direct chemical covalent insertion of small polar moietyes (mainly oxygenated) achieves essential water-soluble fullerences because the peculiar molecular shape of pristine fullerene structures remains substantially preserved. Furthermore, the same covalent polar functionalization that grants hydrophilicity to such structures can be profitably used to provide chemical anchoring sites for appendages to fullerenes paving way for the potential applications of these molecular nanostructures in dendrimer chemistry and self-assembled materials. Unfortunately, such methods have either prolonged reaction times or manifold chemical synthetic steps, with possibly low reaction yields.

However, the promising applications of functionalized high-order fullerenes have not yet been extensively explored particularly for the largest C_n carbon clusters (n>70), although a few such structures are commercially available.

In this study, by a general spectroscopic characterizing approach, we performed the economically efficient rapid synthesis of water-soluble oxygenated derivatives of C_{70} (Fig. 1(a)) and a high-order fullerene mixture (HOFM), containing different mixed upper carbon cluster structures (substantially equivalent extents of C_{76}, C_{78}, and C_{84}, see Figs. 1(b)–1(d)), in accordance to a chemically reductive/air-oxidative reactive protocol, which has been successfully tested for buckminsterfullerene C_{60} its related large polycyclic aromatic

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Fig. 1. The four investigated upper fullerene clusters: fullerene C_{70} (1a); fullerene C_{76} (1b); fullerene C_{78} (the C_{78} isomer is reported) (1c); fullerene C_{84} (D_{2d} isomer) (1d). The last three higher fullerenes constitute the high-order fullerene mixture (HOFM).
hydrocarbons, single-walled carbon nanotubes and graphitized carbon matter. In addition to the synthetic aspects of hydrophilic fullerene chemistry, we intended to explore the oxidizing reactivity of the chemically reduced high-order fullerene carbon clusters, displaying lower structural symmetries with respect to C_{60}, and to compare it with the reactivity displayed by the hitherto reported unsaturated \pi-delocalised carbon frameworks.

2. Materials

C_{70} (98%) and a high-order fullerene mixture (HOFM, i.e., C_{76}, C_{78} and C_{84} at approximately 33%) were purchased from MER Corp (Tucson, Arizona) and used as received. All solvents were purchased from Riedel de Haën. Tetrahydrofuran (THF) was distilled over sodium and benzophenone, then bubbled with Ar for 15 min before use. Deionised water was obtained using a ion-exchange resin. TLC Silicagel60 plates were purchased from Merck.

3. Procedures

In a typical optimized experiment, a suspension of C_{70} (35 mg) was stirred (2 h) in dry THF (15 ml) in a Schlenk tube, in the presence of freshly prepared potassium (0.1 g, i.e., one small slice), in Ar inert atmosphere (CAUTION: any contact of the alkali metal with water and primary alcohols must be rigorously avoided). The reducing activity of potassium, rather than the previously employed liquid alkali alloy Na/K, was experimentally found convenient to handle, given the small quantities of starting fullerenes and reactant metal employed. The mixture slowly turned dark red. Afterwards, air atmosphere was allowed to penetrate the tube, while continuously stirring (4 h). A brown precipitate was formed, and residual potassium was completely decomposed by slowly adding isopropyl alcohol (2 ml) with stirring. By gently mixing, H_{2}O (80 ml) was slowly added afterwards, dissolving the precipitate completely. Due to a by-fraction of decomposed potassium obtained, during the aerobic stage, the yellow-brown alkali solution was neutralized at pH 7 with aqueous HCl. It was concentrated (i.e., evaporated to approximately 20 ml) and an equal volume of CH_{3}OH was added. A brown precipitate was formed, and the mixture was allowed to settle overnight. The pale yellow aqueous solution, containing the formed KCl, was decanted, and the precipitate was dried under vacuum (1 Pa, 2 h, 35°C). The final solid, quantitatively obtained from the starting C_{70} reactant, was found to be a homogeneously hygroscopic, water-soluble powder. The elemental analysis was performed by the SEM-EDX technique, indicating an average carbon/oxygen (C:O) ratio of 6:1.

The same protocol was applied to obtain HOFM water-soluble derivatives (starting from 20 mg of the fullerene mixture). A similar red-brown solid was quantitatively obtained, with an average C:O ratio of 3:1.

As previously reported, the hygroscopicity of water-soluble fullerene derivatives is a limiting factor of the accuracy and reproducibility of analysis results, concerning both the elemental composition and water solubility of the achieved products. However, the reported results indicate the above-mentioned physical and chemical properties of these functionalized structures.
4. Analysis

Infrared solid-state spectra (KBr discs) were collected using a Bruker FTIR Equinox 55 (resolution set at 2 cm⁻¹); Raman solid-state spectra were collected using a Bruker RFS 100 (resolution set at 4 cm⁻¹), equipped with a Nd:YAG laser emitting at 1,064 μm (employed typical laser powers were in the 35–70 mW range). Due to the intense fluorescence background displayed by the pristine HOFM fullerenes (Fig. 4(b)), several packets of scans (for a whole of nearly 10⁵) were accumulated and then averaged. Solution UV-VIS-NIR and solid-state NIR spectra were collected using a Perkin Elmer Lambda 900. For solid-state NIR analysis, solid powders of C₇₀ and water-soluble derivatives were embedded within a 5-mm-wide quartz cell. ¹H-NMR ²H₂O spectra were recorded using a JEOL EX 400 MHz. ¹³C CP-MAS NMR solid-state spectra were recorded using a JEOL GSE 270 spectrometer equipped with a Doty probe operating at 67.9 MHz for ¹³C. Powdered samples were spun at 4–5 kHz. A contact time of 5 ms, a repetition time of 10 s and a spectral width of 35 kHz were used for accumulating 3,000–4,000 transients. ¹³C chemical shifts were referenced via the resonance of external hexamethylbenzene. XRPD spectra were obtained using a Thermo ARL X’TRA 048 X-ray diffractometer, operating with a 1.540562 Å Cu kα₁ radiation as an X-ray source (accelerating voltage, 45 kV; electron current, 40 mA). Energy-dispersive X-ray (EDX) elemental analysis spectra were collected using a SEM/EDX Leo1450 VP scanning electron microscope (gun probe set at a distance of 15 mm; electron acceleration voltage, 20 kV; electron probe current, 3.023 A); the analyses were performed using different 1 mm² portions of 1-mm-thick, 1-mm-diameter powder pellets of the starting fullerenes and water-soluble derivatives. MALDI-TOF MS measurements were acquired using a Bruker Reflex III spectrometer equipped with a nitrogen laser emitting at 337 nm (samples were deposited, employing a 70:30 acetonitrile-water mixture, with 0.2% trifluoroacetic acid, saturated with α-cyano-4-hydroxycinnamic acid, as a laser-assisting matrix; the ion acceleration voltage was set at 25.00 and 20.00 kV, the reflector voltage, at 28.70 and 23.00 kV, and the first extraction plate, at 20.90 and 17.10 kV, for the positive- and negative-ion acquisition modes, respectively).

5. Results and Discussion

Basic spectral information for the characterization of water-soluble fullerene structures is described and compared with the information obtained from the pristine carbon clusters. HOFM, which is a commercial mixture of microcrystalline powders of the upper cluster structures, mainly containing C₇₆, C₇₈ and C₈₄ (at approximately equal amounts of nearly 33%) was utilized. However, C₇₈ and C₈₄ are present as mixtures of their different structural isolable isomers (i.e., three structural isomers of C₂ᵥ, C₂ᵥ’ and D₃ molecular point-group symmetry for C₇₈; basically, two main D₂ and D₂d isomers and five lesser C₂, C(2), D₂d and D₃, plus a minor mixture of D₁₄ and D₁₈ isomers for C₈₄).(46–49) Such a situation accounts for the experimentally observed wide dispersion and overlap of spectral signals.

The elemental analysis performed by the SEM-EDX technique indicates that all fullerene water-soluble isolated products have atomic C:O ratios ranging from 6.59 to 2.51 (averaged recorded values for C₇₀ water-soluble derivatives indicate carbon and oxygen
(C:O) compositions of 85.94% and 14.06%, respectively, while the analysed HOFM water-soluble derivatives indicate C:O compositions of 73.44% and 26.56%, respectively). These results suggest that, on the average, in water-soluble fullerenes the ratio of the number of oxygen atoms to that of fullerene carbon atoms ranges from 1:6 to 1:3, with the more oxygenated high-order structures. The obtained products also display residual KCl, which is the only reaction waste by-product formed during the isolation of hydrophilic derivatives, according to this protocol.\(^{(43–45)}\)

The water-solubility for all derivatives is considerable (about 1 mg/ml in neutral solution for \(C_{70}\) hydrophilic products) and parallels that of \(C_{60}\) water-soluble derivatives, prepared according to the method.\(^{(42)}\) It is perhaps worth noting here that both the employment of a large amount of potassium and a prolonged aerobic oxidation of substrates lead to a generally more oxidized and more hydrophilic mixture of products, whereas a high oxidation rate sensibly enhances the potential molecular fragmentation of cluster cages. Generally, the solubility is moderately affected by the pH of the aqueous solution: basic alkali conditions favour the dissolution of the products (at pH 10, the solubility of \(C_{70}\) water-soluble derivatives reaches about 5 mg/ml), whereas acidic conditions (i.e., from pH \(\leq 5\)) tend to severely hamper it. This behavior, which was observed in similarly treated carbon clusters, chemically mirrors the implantation on the fullerenes of carboxylic units\(^{(42–45)}\) that are reversibly deprotonated or protonated, respectively resulting in a high or low solubility in water, due to their anionic or neutral moiety forms. Similar solubility results and trends were obtained for HOFM hydrophilic derivatives.

Vibrational FT-IR spectra substantially exhibit the typical fingerprinting pattern of ‘classical’ fullerenols which has been observed with water-soluble derivatives prepared by different methods in the literature.\(^{(24,29,30,42)}\) For \(C_{70}\) water-soluble derivatives, the collected spectral results are illustrated in Fig. 2. The four strong bands at 3445, 1637 (asymmetric, (a) FT-IR spectra (KBr discs) of KBr (a), \(C_{70}\) (b) and \(C_{70}\) water-soluble derivatives (c).
with upper shoulders at 1732 and 1670 cm$^{-1}$), 1395 (with an upper shoulder at 1459 cm$^{-1}$) and 1060 cm$^{-1}$ reflect the peculiar presence of oxygenated units on the carbon cage, given the strong intensities of their IR absorption. At 3445 and 1395 cm$^{-1}$, for $\nu$O-H stretching and $\delta$O-H bending modes, respectively, at 1637 cm$^{-1}$ (with its asymmetric profile towards high frequencies) for $\nu$C=O stretching modes and at 1060 cm$^{-1}$ for $\nu$C-O stretching modes, the reported peaks indicate the presence of oxygenated carboxylic, ketonic and alcoholic functions. The vibrational C=C skeletal modes of the carbon clusters in the products are severely hampered by oxidation, because it determines the isomerization of the functionalized structures, with subsequent broadening of fullerene signals embedded within the strongest C=O and O-H modes, within the 1650–1300 cm$^{-1}$ range. Similar results are obtained with HOFM water-soluble derivatives, suggesting that a substantially analogous reactive path is also observed for the higher carbon clusters. The recorded spectra are presented in Fig. 3. Indeed, we have recently collected fairly similar FT-IR spectral patterns for other similarly oxidized different carbon substrates, suggesting that this kind of ‘diagnostic’ spectral profile has to be appropriately referred to a general class of oxidized graphenic structures, on which a different possible set of oxygen functionalities is attached after oxidation.

Conversely, Raman spectroscopy produces more information about the nature of the residual skeletal C=C units of fullerene structures. The acquired results are illustrated in Fig. 4 for the pristine carbon clusters and in Fig. 5 for the oxidized water-soluble products. For the latter, provided with a similar intense fluorescence background, no detectable signals are present within the entire spectral pattern of both hydrophilic derivatives, but the two reported hampered broad absorptions, appreciatively set at about 1600 and 1300 cm$^{-1}$. Such Raman bands are associated with sp$^2$ carbon graphenic units, with the broadening of absorption that reflects the isomerization of structures, occurring after the application of the functionalizing protocol.

![Fig. 3. FT-IR spectra (KBr discs) of KBr (a), HOFM (b) and HOFM water-soluble derivatives (c).](image-url)
In addition, we have performed a solid-state NIR study\textsuperscript{(53)} for C\textsubscript{70} water-soluble derivatives, comparing data that were obtained for the pristine carbon structures and the functionalized products. The results are reported in Fig. 6. The absorptions of C\textsubscript{70}\textsuperscript{(54)} detected by fullerene bulk analysis, due to vibrational overtones and combination modes of the peculiar C\textsubscript{70} spectral pattern, in the hydrophilic derivatives appear submerged within a continuum of absorption in the 1000–2500 nm range. This indicates a wide extent of structural isomerization after chemical functionalization. The only clearly visible peaks in Fig. 6(b) are associated with the strong absorption at about 1940 nm and with the less intense
broad peak at approximately 1440 nm, which are due to water molecules absorbed on oxygenated fullerenes, because of their hygroscopic tendency.\textsuperscript{(55)}

The \textsuperscript{1}H NMR spectrum of C\textsubscript{70} water-soluble derivatives (recorded in deuterated water basified at approximately pH 10 with deuterated sodium hydroxide) does not indicate any hydrogen atom belonging to oxygen groups, reasonably because of the rapid exchange between such mobile protons and the deuterated solvent. It is perhaps interesting to observe the series of smoothed broad peaks within the 2.2–0.8 ppm range, which are consistent with a minor dispersion of protons directly attached to the cluster cage. The parallel \textsuperscript{13}C NMR solution spectrum in the same solvent reveals the wide extent of fullerene sp\textsuperscript{2} carbon atom chemical shifts achieved after reaction. It shows a very broad hump centred at about 140 ppm.\textsuperscript{(56)} The dispersion of signals prevents the reliable assignment of the oxygen-linked carbon atoms. The solid state \textsuperscript{13}C CP MAS NMR spectrum of these products is shown in Fig. 7. A strong broad overlap of absorptions within the 150–110 ppm range accounts for the sp\textsuperscript{2} carbon moieties isomerized after the oxidation of the fullerene frame (chemical shift resonances for fullerene C\textsubscript{70} are observed at 151.4, 148.8, 148.1, 146.2 and 131.7 ppm).\textsuperscript{(57)} The nearly negligible absorption within the 180–160 ppm range is tentatively associated with the presence of carbonyl atoms, respectively belonging to ketonic and carboxylic moieties. These spectral features were instead rather well observed by the NMR technique for C\textsubscript{60} and decacylene water-soluble derivatives, as well as by the XPS technique for SWNT water-soluble derivatives, suggesting that in the present case the reactive path tends to mostly favour the hydroxylation of structures, rather than the introduction of ketonic and carboxylic moieties. The most evident presence of an absorption centred at about 70 ppm and assignable to tertiary alcoholic carbon units\textsuperscript{(58)} strengthens this observation, confirming the preponderant extent of hydroxylation for the present substrate. It is worth noting the imposing absorption in the 40–20 ppm range, compatible with hydrogenated sp\textsuperscript{3} carbon atoms.\textsuperscript{(58)} This result in functionalized carbon substrates has been previously substantially
overlooked, due to hydrocarbon contaminations, from general spectral evidences,\(^{(42,43)}\) or partially to an extent of keto-enolic tautomeric equilibrium in oxidized carbon substrates.\(^{(44,45)}\) In view of this recent result, it might be feasible to consider that a partial hydrogenation on graphene carbon surfaces takes place as a direct result of this synthetic methodology.

The UV-VIS spectra (Fig. 8) of water-soluble products are considered another typical hallmark of these oxidized substrates. All spectra are dominated by prominent electron absorption, showing the peak centred in the narrow 190–200 nm range, as it is expected for the electron transitions of oxygen moieties,\(^{(59)}\) and preceded by a variable gradual constant decrease in transmittance. The slope of the curve in this upper wavelength zone appears to be intrinsically dependent on the degree of electron absorption provided by the remaining unsaturated C=C bonds, and therefore, on the actual extent of surface oxidation of carbon substrates.\(^{(45)}\) Indeed, we found that water-soluble products, achieved by reacting fullerenes with a small amount of the metal-reducing agent, resemble a UV-VIS spectrum in which a gradual increase in absorption is observed, as reported, \(e.g.,\) in Fig. 8(a). Conversely, a large amount of the reducing agent yields (because of the massive oxidation) a more transparent profile within the upper UV-VIS zone, with a sharp decrease in transmittance reached in the near proximity of the oxygen-unit absorption area (i.e., the situation proposed for the HOFM water-soluble derivatives shown in Fig. 8(b).
XRPD spectra analysis was performed on both C\textsubscript{70} and HOFM water-soluble products and their respective fullerene precursors.\cite{60} The obtained results are illustrated in Figs. 9 and 10. The only visibly crystalline diffraction pattern for products is due to the contaminant reaction by-product KCl (for HOFM, there are also peaks referred to NaCl, since NaOH was used to adjust the pH during the isolation of derivatives).\cite{44,45} In all oxidized substrates, regardless of the crystal lattice of the starting reactant fullerenes, the isomerization induced by oxygen atom attachments invariably leads to markedly carbonaceous amorphous products, without any diffraction pattern to suggest any extent of the solid-state crystalline order of the functionalized fullerene carbon frameworks.

In all the achieved products, the mixture of isolated isomers shows substantially a chromatographic homogeneous retention time. The TLC elution of both C\textsubscript{70} and HOFM derivatives in the Silicagel\textsubscript{60} stationary phase with a 3:2 water/methanol mixture (NaOH, pH 9) resulted in only one wide brown eluting band, progressively broadening during the elution. The observed small forefront fraction is reasonably assigned to the partial extent of the decomposition product due to the collateral fragmentation side reaction.

However, MALDI-TOF MS spectra were recorded in order to obtain information about the molecular weights and isomeric dispersion of the functionalized fullerenes. Figure 11 shows an exemplified result, in which HOFM water-soluble derivatives are intensely detected,\cite{29} albeit the poor solubility of these hydrophilic products in the solvent mixture used to deposit samples for analysis. Partial fullerene carbon cage fragmentation is observed.

The exposure of chemically reduced carbon structures to atmospheric oxygen has been proved to afford highly oxidized carbonaceous substrates.\cite{42-45} The oxidizing role of electrophilic O\textsubscript{2} provided by aerobic atmosphere has been verified to be active in C\textsubscript{60} fullerene frames.\cite{27} However, according to this proposed protocol, the preceding chemical
electron reduction\(^{(61)}\) greatly enhances the oxidation of the cluster carbon frames.\(^{(62)}\) The electron reduction of fullerenes is verified by observing the NIR spectra of THF solutions of carbon clusters stirred in the presence of potassium, as reported in Fig. 12. For C\(_{70}\), the peculiar absorption at 1372 nm indicates the presence of the fullerene monoanion\(^{(63,64)}\) within the reacting mixture, whilst the other peaks observed at 782, 896 and at 1071 nm are reasonably ascribed to partial fullerene oxidation, due to the high reactivity exhibited by the cluster;\(^{(65)}\) similarly, for HOFM the weak absorptions recorded at 803, 855, 977 and 1260 nm are well consistent with the electron transitions exhibited by reacting reduced fullerenes.
Fig. 11. MALDI-TOF spectrum (positive ion acquisition mode) of HOFM water-soluble derivatives.

Fig. 12. NIR solution spectra (THF) of K-reactant C_{70} (a), C_{70} (b), K-reactant HOFM (c) and HOFM (d).
In fact, different from the previously reported $\text{C}_{60}$ water-soluble derivatives, a high quantitative reactivity\textsuperscript{(66)} for all the charged higher carbon clusters is observed. Moreover, the hydroxylation of structures appears to be by far the most predominant effect of the reaction, rather than the carboxylation or carbonylation of frames. This result can be rationalized by considering that the substantially variable bond length of the upper fullerenes,\textsuperscript{(67)} diversely from that exhibited by ‘spherical’ $\text{C}_{60}$, actually leads to the localization of carbon-carbon double bonds, particularly in the polar regions of their structural frames. Hence, reduced clusters are rendered more reactive towards electrophilic oxidizing reactions\textsuperscript{(66)} and reasonably more likely to attach simple oxygen moieties such as hydroxyls, rather than promoting reactive cage rearrangements and carbon-carbon bond breaking, as it is due to the formation of ketonic and carboxylic moieties. However, experimental spectral data clearly indicate the presence of different oxygen groups attached to fullerene cages, as well as a small extent of cluster hydrogenation. In particular, the presence of a small number of carboxylic moieties, which was weakly detected by spectroscopic techniques, appears to well mirror the peculiar pH-dependent behavior exhibited by hydrophilic derivatives, being consistent with the final result of oxidative cleavages of carbon-carbon bonds, which is clearly suggested by the partial cluster fragmentation observed in MS spectra. Within this context, carboxylic groups have been clearly detected in other hydrophilic derivatives of analogous carbonaceous substrates, after the application of the present oxidizing protocol.\textsuperscript{(42,45)} With respect to other reactive oxidizing protocols reported for $\text{C}_{60}$,\textsuperscript{(24–29)} this aerobic method appears feasible due to its effective fastness and simplicity. Conversely, it seems to enhance the potential partial fragmentation of the cluster cages;\textsuperscript{(42,44)} however, this aspect can be interestingly involved in the insertions of both ketonic and carboxylic moieties in fullerene frames.

Therefore, a tentative representation of one possible isomeric structure for $\text{C}_{70}$ water-soluble derivatives is illustrated in Fig. 13, while details about a general schematic reactive path for fullerene structures, as previously reported, are suggested in Fig. 14. A supplementary collateral mechanism, involving the role of $\text{H}_2\text{O}$, provided by atmospheric air moisture, in the observed partial protonation of these highly reactive reduced structures is proposed in Fig. 15.

![Fig. 13. Tentative structural model for possible isomer of $\text{C}_{70}$ water-soluble derivatives. The polar regions of the fullerene frames are preferentially functionalized by the attachment of different oxygen groups to the cluster cage. A partial hydrogenation is illustrated. Note that the insertion of C=O motifs can induce partial fullerene fragmentation.](image-url)
The metal agent, then, massively promotes both the initial \( \text{O}_2 \) attachments and the progressive extensive oxidation of clusters. Moreover, the importance of the metal-reducing agent during the second aerobic oxidative step is strengthened by the experimental trials, performed using only a nearly stoichiometric quantity of K. In such a case, not all the fullerene reactant matter is water-solubilized, leaving a large amount of only partially oxidized structures that do not display any marked hydrophilicity. Conversely, using an increasing amount of metal-reducing K, highly water-soluble products are obtained with a resulting UV-VIS spectrum (see Fig. 8(b)) that explains the substantial disappearance of the
absorptions within the 220–500 nm range, due to C=C delocalised unsaturations; the fullerene products are highly oxidized by massive oxygen cage attachments. However, it must be noted that an excessive amount of the reducing agent consequently leads to a consistent extent of structural fullerene fragmentation, particularly for the more reactive high-order fullerenic frames. Therefore, the optimized balance between these opposite trends must be experimentally adjusted.

6. Conclusion

In this study, a very simple rapid efficient method for the quantitative achievement of water-soluble fullerene higher clusters has been proposed. The obtained products displayed both a high hydrophilicity and a moderate pH-sensitive behaviour, due to a massive isomeric covalent insertion of hydroxylic, ketonic and carboxylic oxygen groups in fullerene carbon cages. The oxidized fullerene clusters were comprehensively characterized by several different spectroscopic techniques that concurred in elucidating a general peculiar spectral background for these functionalized substrates. The described one-pot method is remarkably feasible due to its simplicity and the quantitative yields of hydrophyllic products achieved. In particular,

• the oxidation of fullerenes is suggestively provided by atmospheric oxygen,\(^{(27)}\) whose insertion in clusters is highly favoured by the previous chemical reduction of the carbon frames, employing an alkali-metal-reducing agent;
• hydroxylation appears to be by far the most predominant result of the oxidation process, as a result of the reactivity of the investigated chemically reduced fullerenes;
• spectral data seem to suggest a minor side reaction of hydrogenation for the fullerene frames, with the possible involvement of atmospheric moisture;
• the fullerene structural strain combined with little bond alternation displayed by the higher carbon clusters in their polar regions may induce the resolute reactivity of these
structures, determining both the high reaction velocity and the complete conversion of reactants into functionalized products;
- the attuned use of the alkali-metal-reducing agent promotes an optimized oxygen insertion in fullerene frames, maximizing water solubility and minimizing cluster fragmentation during the dispersion of the achieved isomeric products.

Further studies, conjugated with the commercial availability of pure higher fullerene allotropes, may be directed toward the development of an appropriate quantitative separation method, in order to isolate specific higher fullerene hydrophilic derivatives and better discriminate the manifold possible generated isomers in the mixture.

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