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Fullerenes and fullerenols survival under irradiation

V. A. Shilin, A. A. Szhogina, M. V. Suyasova, V. P. Sedov, V. T. Lebedev, V. S. Kozlov

National Research Centre “Kurchatov Institute” B. P. Konstantinov, Petersburg Nuclear Physics Institute, 188300, Russia, Leningrad district, Gatchina, Orlova Roscha, Russia

shilin@pnpi.spb.ru

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Fullerenes C_{2n}, endometallofullerenes Gd@C_{2n}, Gd@C_{82} and water-soluble Gd@$C_{2n}(OH)_{38-40}$ derivatives were synthesized. These substances’ survival dependences on the accumulated flux (10^{16} – 10^{19} neutron/cm^2) of neutron irradiation over a wide spectrum of energies (from thermal to fast) in the WWR-M reactor zone (Petersburg Nuclear Physics Institute) have been examined.

Keywords: fullerenes, endometallofullerenes, fullerenols, irradiation, survival.

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1. Introduction

Radiochemical technology allows the creation of new carbon-based materials and the study of their properties, stability and structure. The application of radiolabeled fullerenes, endohedral metallofullerenes (EMFs) and their water-soluble derivatives is of particular importance in modern nuclear medicine and biology, due to their potential utility as radiopharmaceuticals. Fullerene and EMF functionalization, by the attachment of different groups permits the targeted delivery of drug molecules and the use of radioactive EMF properties for diagnostic and therapeutic purposes. There are many published reviews describing endohedral fullerenes and methods for their preparation, for example [1-3].

Recent results from stability studies of endofullerenes and their water-soluble derivatives undergoing irradiation by fast and thermal neutrons in the reactor WWR-M (PNPI) are presented in this article. Non-phonon excitation mechanisms were proposed for understanding the fullerenols’ interactions with fast neutrons. In particular, fast electron shaking is suggested as the most probable process [4,5].

It is clear that EMFs irradiations at different neutron fields may lead to their destruction and cause the formation of new chemical substances. A molecule with daughter nucleus may also change the original chemical form leading to such instabilities as oxidation, degradation, crosslinking, etc. For example, there can be a reaction with oxygen due to ionizing radiation accompanied by the formation of reactive radical intermediates.

Although the stabilities of fullerenes and EMFs have been thoroughly investigated [6-9], the stabilities of water-soluble fullerene derivatives are less documented. This is why the present investigation is necessary.

The studies seem to be very prospective for advanced medical applications of metallofullerenes and their isotopic forms for the diagnostics (MRI) and tumor therapy. The active component (heavy metal, isotope) in such molecules is screened from surrounding tissues and toxicity risks are minimized.

2. Experimental and discussions

The substances in the series (C_{2n}, Gd@C_{2n}, Gd@C_{82} and Gd@$C_{2n}(OH)_{38-40}$) were synthesized for these studies. The fullerene-containing soot was produced by subjecting graphite rods to electric arc treament. Subsequently, the soot was extracted with o-xylene. The C_{2n} extract's composition was determined by high-performance liquid chromatography (HPLC).

High purity (99 %) sample Gd@C_{82} was extracted from soot using the solvents o-xylene and N,N-dimethylformamide (DMF). The subsequent transfer of DMF in o-xylene allows the use of chromatographic separation and final Gd@C_{82} purification [10,11].

The Gd@C_{2n} fullerenes were isolated from soot using DMF extraction with the addition of a reducing agent to enhance the ability of the extractant. The Gd@C_{2n} obtained in this manner was the initial compound to yield the hydroxylated Gd@$C_{2n}(OH)_{38-40}$ sample in dilute aqueous hydrogen peroxide solution at 65°C. According to X-ray fluorescence analysis (XRF), water-soluble fullerenols contained 4.8 wt% of gadolinium. The number of hydroxyl groups in a fullerenol molecule (x = 38–40) was determined gravimetrically (thermal analysis [12]). The resulting product contained 55% of the gadolinium component according to calculation based on the Gd@$C_{82}(OH)_{38}$ formula.

The powder samples were soldered in quartz ampules and irradiated for 0.5 – 32 h in integral flux of up to 10^{19} neutrons/cm^2 in the WWR-M. The temperature in the reactor channel was 70 °C.

The irradiated samples stability was determined as follows: the water soluble Gd@C_{2n} $(OH)_{38-40}$ was dissolved in a determined volume of water, assuming the previously-determined solubility. The solution was then stirred for 4 h at 25 °C and was then centrifuged. Irradiated C_{2n}, Gd@C_{2n} and Gd@C_{82} samples were dissolved in o-xylene and stirred for 24 h. The insoluble precipitates were dried and weighted. The differences between the C_{2n} original weights and the insoluble portions, normalized to the initial weights provided product stability data. The stability was defined for the Gd@$C_{2n}(OH)_{38-40}$, Gd@C_{2n} and Gd@C_{82} samples as the radioactivity ratio for the soluble and insoluble portions.

A Shimadzu LC-20 HPLC with Lab Solutions software and system for data processing and output analysis was used for both analysis and separation. The fullerene fractions separation and final purification were performed using three types of chromatographic columns: a BuckyPrep 4.6 × 250 mm analytical column, a Buckyrep 10 × 200 mm semi-prep column, and a Buckyrep 10 × 200 mm semi-prep column. Pure toluene was used as a mobile phase (eluent) in standard analyses. The peaks were detected by the absorption at 330 nm.

Mass-spectrometric analysis of the high-purity Gd@C_{82} sample was performed with a Varian Fourier transform ion cyclotron resonance mass spectrometer and with an Ultraflextreme device (Bruker), respectively. The Gd@C_{82} sample spectra were recorded at standard device tuning (500 – 4500 Da) without the use of a matrix. The positive ions were recorded at a minimal laser power near the ion appearance threshold, so as to suppress the possible fragmentation. The obtained mass-spectrum is shown in Fig. 1.

Chemical bonding information on the hydroxyl groups was obtained using Fourier transform infrared spectroscopy (FTIR). The measured product FTIR-spectrum showed characteristic frequencies corresponding to chemical bonds in fullerenols. The spectrum is dominated by a broad band at 3412 cm^{-1}, presumably due to the stretching mode of the OH-groups, as well as other peaks at 1620 cm^{-1} (C=C), 1390 cm^{-1} and 1150 cm^{-1} (C–OH).

The γ-spectra were recorded using a semiconductor spectrometer with a detector based on high-pure germanium HPGe (Ortec, EG & G) as done in previous work [13]. The detector

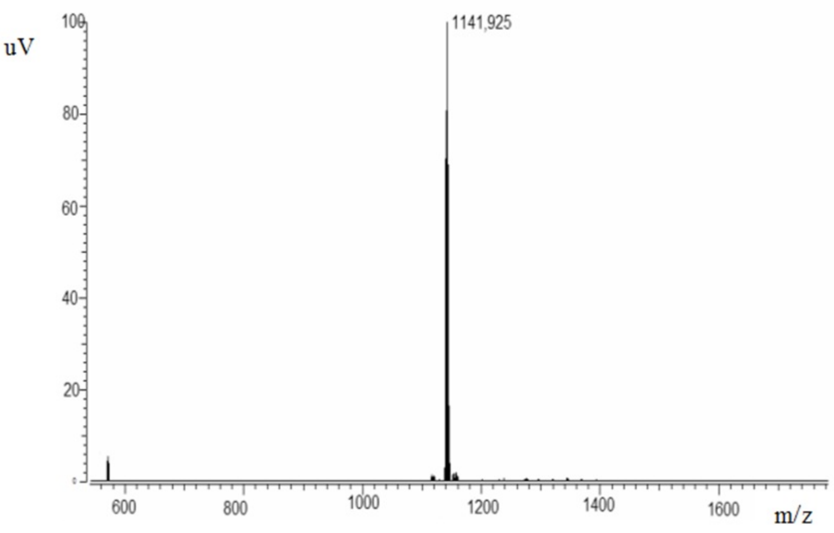


FIG. 1. Mass-spectrum of Gd@C_{82}, Varian mass-spectrometer

efficiency for the 1 MeV range was 5 %. Resolution for 122.06 keV γ-line of ^{57}Co was 0.57 keV. The diameter of the detector was 25 mm and the thickness was 13 mm.

The stability dependence of C_{2n}, Gd@C_{2n}, Gd@C_{82}, Gd@$C_{2n}(OH)_{38-40}$ upon irradiation time is shown in Fig. 2.

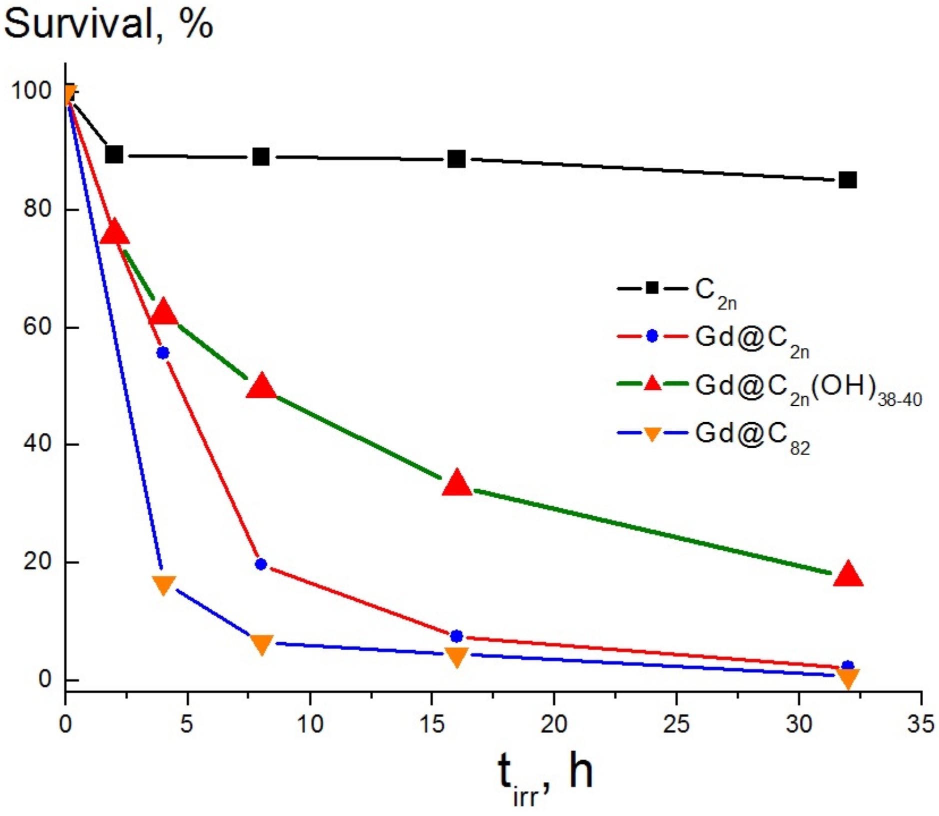
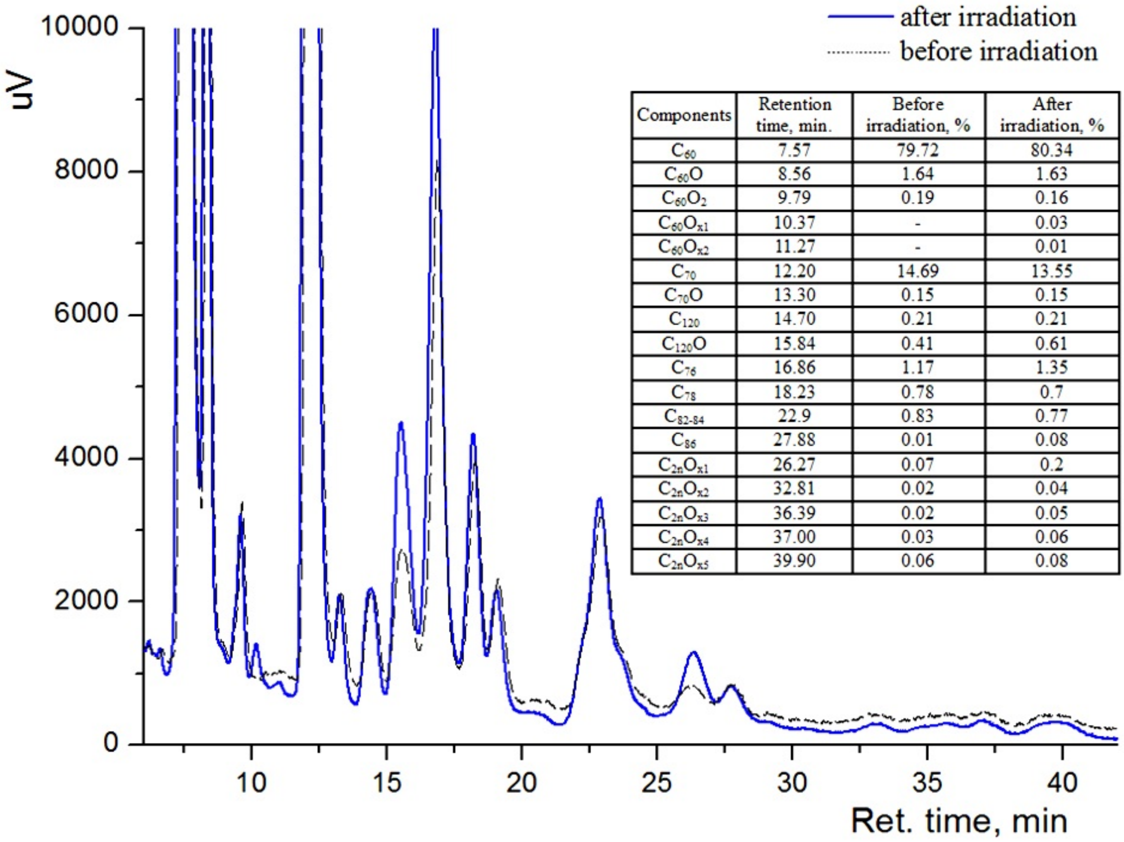


FIG. 2. The fullerenes and fullerenols stability dependence upon irradiation time at an integral flux of $8 \cdot 10^{13}$ neutron/s·cm^2

As it can be seen in Fig. 2, the C_{2n} fullerenes have the higher survival as compared with others. It is no wonder, since the C_{2n} composition (Fig. 3) contains predominantly C_{60} and C_{70} [14] possessing a high survival.



Components	Retention time, min.	Before irradiation, %	After irradiation, %
C_{60}	7.57	79.72	80.34
$C_{60}O$	8.56	1.64	1.63
$C_{60}O_2$	9.79	0.19	0.16
$C_{60}O_{x1}$	10.37	-	0.03
$C_{60}O_{x2}$	11.27	-	0.01
C_{70}	12.20	14.69	13.55
$C_{70}O$	13.30	0.15	0.15
C_{120}	14.70	0.21	0.21
$C_{120}O$	15.84	0.41	0.61
C_{76}	16.86	1.17	1.35
C_{78}	18.23	0.78	0.7
C_{82-84}	22.9	0.83	0.77
C_{86}	27.88	0.01	0.08
$C_{2n}O_{x1}$	26.27	0.07	0.2
$C_{2n}O_{x2}$	32.81	0.02	0.04
$C_{2n}O_{x3}$	36.39	0.02	0.05
$C_{2n}O_{x4}$	37.00	0.03	0.06
$C_{2n}O_{x5}$	39.90	0.06	0.08

FIG. 3. Fullerenes C_{2n} chromatogram

Meanwhile, the $Gd@C_{2n}(OH)_{38-40}$ has shown a higher survival compared with $Gd@C_{2n}$ and $Gd@C_{82}$. This stability of fullerenol can be interpreted as the effect of its shell containing OH-groups and absorbed water. Really thermal neutrons undergo very intense incoherent scattering on the protons in the shell of fullerenol that prevents neutron absorption by the gadolinium atoms and the subsequent cage destruction due to recoil.

$Gd@C_{2n}$ survives better than $Gd@C_{82}$, because it contains mainly C_{60} which has a more stable framework and lower amounts of higher fullerenes such as C_{82}. This testifies to the fact that the main reason for EMF destruction is a result of the Szilard-Chalmers reaction.

The high survival of $Gd@C_{2n}$ sample as compared to $Gd@C_{82}$ can be associated with a difference in metal atom localization inside the carbon cage, with the electron-donating properties of the surrounding molecular environment and etc. It is known that the EMF properties are strongly dependent upon the metal atom's position inside the carbon cage. It has been noted that even a slight shift inside the carbon atom framework can lead to significant changes in the EMF's molecular properties [15-18].

It should be noted, there is a substantial charge transfer between Gd and the nearest carbon atoms in a $Gd@C_{82}$ molecule. This value was found to be almost 2.5 times higher than in $La@C_{82}$ molecule [19]. Such a high charge density suggests a strong bonding for Gd with the nearest carbon atoms (i.e. covalent bonds). Obviously, this circumstance makes the molecule $Gd@C_{82}$ and $Gd@C_{2n}$ more resistant to various physical and chemical, and, in our opinion, radiation effects. It should be noted that the charge transfer of Gd, and La are drastically different, even though they have very similar oxidation potentials Mo^0/M^{3+} (-2.4 V). It is known that with such potential lanthanides donate three electrons to the fullerene cage and become trivalent.

In EMF molecules and their derivatives [20-22] the electron structure is modified not only via an internal charge transfer but also due to exterior effects, for example, by the presence of attached hydroxyl groups. For fullerenes, EMF and fullerenols such a combination makes the treatment of their resistance to irradiation very complicated and dependent on molecular symmetry, size, carbon framework electronic structure, the atom's localization inside a carbon cage, the atom's recoil energy, and at last on the presence of impurities and damage in the irradiated material.

It is worth noting that except for destruction, the irradiation may induce opposite processes, i.e. a synthesis of some molecular forms. When the recoil high-energy metal atom can leave molecule and then collide with other molecules to destroy them, this recoil energy of the atom is reduced and it can insert itself into another carbon cage, thus creating a new EMF.

Table 1 shows some previously obtained endometallofullerenols' stability data under different conditions. Such factors are the samples' composition, the metal atom radius, the nuclear recoil energy upon neutron capture. Although the various factors cumulative effect greatly smoothes, the presence $C_{2n}(OH)_x$ fullerenol influence apparently predominates.

TABLE 1. The endometallofullerenols survival dependence from different factors [23]

Element	Mixture content, %		Atom radius, pm	Recoil energy, eV	Survival, %
	$M@C_{2n}(OH)x$	$C_{2n}(OH)x$			
Sm**	17 ($Sm@C_{2n}$)	83 (C_{2n})	181	237	85
Tb	81	19	180	136.1	52
Gd	60	40	179	136.4	94.1
Sc	95	5	162	894.1	82.5
Fe	97,6	2,4	126	393.3	47.0
Mo	12	88	139	123.0	87.2
Pr	70	30	182	126.9	45.0
C_{2n}	–	100	–	–	85

*The samples irradiation are proceeded during 8 h in the integral flux $8{\cdot}10^{13}$ neutron/s·cm^2.

** The sample $Sm@C_{2n}$ survival is shown for comparison. The irradiation are proceeded during 2 h in the integral flux $8{\cdot}10^{13}$ neutron/s·cm^2 [24].

Another feature of endometallofullerenols behavior under neutron irradiation is the relatively high stability value as compared to the EMF. As it is seen from Table 1, all fullerenols showed significantly greater stability (from 45 to 94 %) than the corresponding $M@C_{2n}$ (from 15 to 20 %). We expected to obtain similar results for irradiated C_{60}, C_{70} fullerenes and $C_{60}(OH)_x$, $C_{70}(OH)_x$ water-soluble derivatives [14]. However, comparison of the stabilities of C_{60}, C_{70} with their water-soluble derivatives of $C_{60}(OH)_x$, $C_{70}(OH)_x$ shows that fullerenol survival decreases by 2 – 3 times under 32 h irradiation as compared with fullerenes. Fullerenol molecules under irradiation lose some of the hydroxyl groups and are not destroyed, becoming insoluble. The soluble part weight reduces. The soluble and insoluble parts comparison becomes incorrect. Therefore additional investigations are nesessary.

Previously investigated samples M@C_{2n} (M = Sc, La, Nb, Sm, Eu, Tb, Ho, Yb, Tm, Lu, Pr, Fe, Mo, Gd) have shown the average survival from 15 to 20 % except Sm@C_{2n} and Gd@C_{2n} [24]. As mentioned earlier, a Gd@C_{2n} high stability to reactor neutron irradiation can be explained by an abnormal feature of Gd-endohedral fullerene's electronic structure. The high stability of Sm@C_{2n} can also be explained in such a way. To determine the anomalous features of how the bivalent Sm^{+2}@C_{2n}^{-2} differs from Gd^{+3}@C_{2n}^{-3}, additional investigations are nesessary. Although one should bear in mind that under certain circumstances, the bivalent Sm^{+2} can be transformed into trivalent Sm^{+3} [25].

3. Conclusion

The C_{2n} fullerenes, Gd@C_{82}, Gd@C_{2n} endofullerenes and Gd@$C_{2n}(OH)_{38-40}$ water-soluble derivatives were synthesized, purified and a comparative analysis of their stabilities under neutron irradiation has been performed at the PNPI WWR-M reactor.

Various factors have defined the fullerenes' and fullerenols' stability to neutron irradiation; among these factors are the Szilard-Chalmers reactions and electronic structural features which give the largest contribution to these compounds' destruction.

The survival of water-soluble Gd-fullerenol was found to be an order of magnitude greater than that of the original EMF which is of substantial importance, assuming fullerenols' biomedical applications as advanced isotopic preparations.

In general, the investigation of fullerenes and fullerenols behaviors under irradiation carries not only theoretical but predominantly practical interests, since the knowledge of their radiation resistance offers a suitable option for a variety of the aforementioned biomedical applications.

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