Encapsulation of Radioactive ^{159}Gd and ^{161}Tb Atoms in Fullerene Cages

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We demonstrate a novel form of metallofullerenes, namely, those with radioactive atoms encapsulated in the C_{82} cage. The metal atoms were made radioactive by a neutron capture reaction or through a nuclear decay process. The most important and intriguing finding of the present study is that the endohedral form of metallofullerenes is not affected by the recoil energy of the metal atom resulting from emission of electrons in the β decay. Such a stability of the cage against the recoil energy of the encapsulated atom was confirmed by the elution behavior of the metallofullerene in liquid chromatography. Successful encapsulation of radioactive atoms inside the fullerene cage will greatly widen the potential use of endohedral metallofullerenes not only in basic science and technology but also in other areas, such as medicine.

Following the report on a macroscopic quantity of metallofullerenes,[1] several milligram quantities of La atoms encapsulated in the C_{82} cage have successfully been isolated very recently,[2,3] and the task of their characterization has just begun.[2-6] All the experimental and theoretical evidence accumulated so far has strongly supported the presence of the metal atom inside the C_{82} cage and, thus, the chemical activity of the metal being severely suppressed.[1-6] Indeed the isolated sample can survive under air for at least a half year.

The soot for $Gd@C_{82}$ was prepared by arc heating of a graphite containing Gd oxide of natural isotopic abundance, and fullerenes with $Gd@C_{82}$ were extracted using CS_2. Isolation of $Gd@C_{82}$ from the crude extract was carried out by the two-step HPLC method,[2,7] and it was found that $Gd@C_{82}$ in toluene with a polystyrene column (JAIGEL 2H × 2, 20 × 600) was eluted within a single peak at around 105 min, as shown in the inset of Figure 1, similar to $La@C_{82}$.[2,8] Another portion of the crude extract was irradiated by neutrons in a TRIGA MARK II reactor of the Institute for Atomic Energy, Rikkyo University, at a neutron

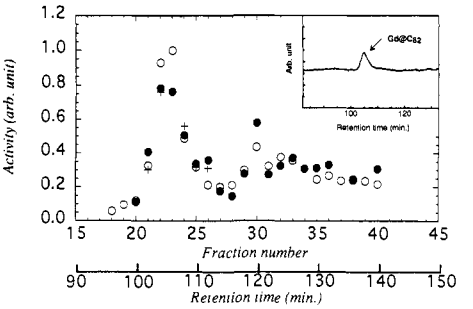

Figure 1. HPLC elution curves of the soluble portion of the neutron-irradiated crude extract. Toluene was used as an eluent with a polystyrene column at a flow rate of 5 mL/min. The inset is an elution curve of purified $Gd@C_{82}$ measured by UV absorption at $\lambda = 290$ nm under the same conditions as those for the radioactive crude extract. The radioactivity of ^{159}Gd (○), ^{161}Tb (●), and ^{153}Gd (+) for 60 fractions was determined by energy-resolved γ-ray counting (E_γ = 363.6, 74.6, and 97.5 keV), respectively. Radioactivities of ^{161}Tb and ^{153}Gd for each fraction were normalized to that of ^{159}Gd by using ratios $^{161}Tb/^{159}Gd$ and $^{153}Gd/^{159}Gd$ for a standard Gd nitrate irradiated under the same conditions as the crude extract.

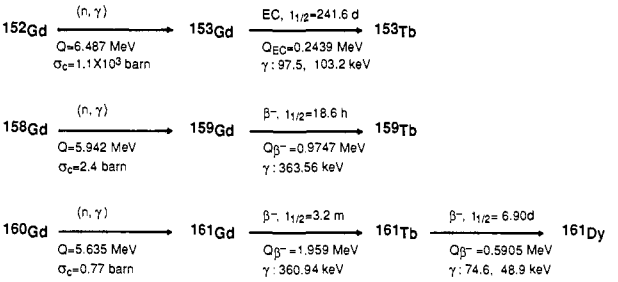

Figure 2. Nuclear reaction and decay process related to ^{159}Gd, ^{161}Tb, and ^{153}Gd.[9]

flux of 1.5×10^{12} n cm^{-2} s^{-1} for the activation of Gd isotopes. After 6 h of irradiation, the sample was first transferred to a vial by CS_2 for the determination of total ^{159}Gd radioactivity by a Ge γ-ray detector. The CS_2 solution was then filtered to remove insoluble materials with a membrane filter (pore size, 0.45 μm). The γ-ray measurement of the dissolved fraction revealed that almost 90% of ^{159}Gd remained in the insoluble fraction, which would be ascribed to the effect of the recoil energy (as much as 119 eV) associated with the prompt γ-ray emission following the neutron capture.

After removal of CS_2 by evaporation, the soluble fraction was dissolved in toluene and injected into HPLC. The eluent was divided into 60 fractions, each being collected for 2 min after the first 60 min portion was discarded. The results of γ-ray measurements of each fraction are shown in Figure 1 for the nuclides ^{159}Gd, ^{161}Tb, and ^{153}Gd, and the nuclear reaction and decay data related to these three isotopes[9] is given in Figure 2. As the radioactivity of ^{153}Gd was little, it could only be measured in several fractions. In Figure 1, at least one distinct elution peak is observed at fractions 22 and 23, which correspond to the retention time of 105 min. It is noted that the peak position of ^{161}Tb exactly coincided with those of ^{159}Gd and ^{153}Gd. This observation corroborates the formation of $^{161}Tb@C_{82}$ following the β decay of $^{161}Gd@C_{82}$ during and soon after the neutron irradiation. (The irradiated sample was cooled for 4 h before the chemical treatment described above.)

In order to study the stability of the C_{82} cage against the perturbation caused by neutron capture and β decay, ratios of the sum of the γ counts observed in fractions 21–24, $^{153}Gd/^{159}Gd$ and $^{161}Tb/^{159}Gd$, were evaluated and compared with those

(1) Chai, Y.; Guo, T.; Jin, C.; Haufler, R. E.; Chibante, L. P. F.; Fure, J.; Wang, L.; Alford, J. H.; Smalley, R. E. *J. Phys. Chem.* **1992**, *95*, 7546.
(2) Kikuchi, K.; Suzuki, S.; Nakao, Y.; Nakahara, N.; Wakabayashi, T.; Shiromaru, H.; Saito, K.; Ikemoto, I.; Achiba, Y. *Chem. Phys. Lett.* **1993**, *216*, 67.
(3) Bethune, D. S.; Johnson, R. D.; Salem, J. R.; de Vries, M. S.; Yannoni, C. S. *Nature* **1993**, *356*, 123.
(4) Suzuki, T.; Maruyama, Y.; Kato, T.; Kikuchi, K.; Achiba, Y. *J. Am. Chem. Soc.* **1993**, *115*, 11006.
(5) Hino, S.; Takahashi, H.; Iwasaki, K.; Matsumoto, K.; Miyazaki, T.; Hasegawa, S.; Kikuchi, K.; Achiba, Y. *Phys. Rev. Lett.* **1993**, *71*, 4261.
(6) Poirier, D. M.; Knupfer, M.; Weaver, J. H.; Andreoni, W.; Laasonen, K.; Parrinello, M.; Bethune, D. S.; Kikuchi, K.; Achiba, Y. *Phys. Rev. B Phys. Rev.* **1994**, *B49*, 17403.
(7) Kikuchi, K.; Nakao, Y.; Wakabayashi, T.; Achiba, Y. In preparation.
(8) Sueki, K.; Kobayashi, K.; Kikuchi, K.; Tomura, K.; Achiba, Y.; Nakahara, H. *Fullerene Sci. Technol.* **1994**, *2*, 213.
(9) Lederer, C. M.; Shirley, V. S., Eds. *Table of Isotopes*, 7th ed.; John Wiley & Sons, Inc.: New York, 1978.

0002-7863/94/1516-9775$04.50/0

observed for a standard Gd nitrate sample which was irradiated with the crude extract in the same irradiation capsule. The obtained ratios $^{153}Gd/^{159}Gd$ and $^{161}Tb/^{159}Gd$ were 0.0133 ± 0.0005 and 0.039 ± 0.002 for the sample of fractions 21–24 and 0.0153 ± 0.0008 and 0.043 ± 0.003 for the standard, respectively. The distribution of the recoil energy of the metals inside the cage due to the prompt γ-ray emission following neutron capture cannot be calculated because of a lack of sufficient γ-ray data, but the maximum recoil energies expected from the Q values of neutron capture reactions are 119 and 148 eV for ^{159}Gd and ^{153}Gd, respectively. The fact that the ratios $^{153}Gd/^{159}Gd$ are almost the same for the sample and the standard shows that the difference of the maximum possible recoil energy between the two neutron capture reactions is not significant for the survivability of Gd@C_{82}. Therefore the agreement of the ratios $^{161}Tb/^{159}Gd$ for the sample and the standard shows that the C_{82} cage was little affected by the recoil energy of ^{161}Tb due to the β decay (see Figure 3 for the expected recoil energy distribution) or by the rearrangement of the electronic states due to the sudden change of the nuclear charge from 64 to 65. Stability of the fullerene cage against the recoil energy of less than 14.6 eV is in agreement with the reports on the decomposition of the fullerene cages by ions or photons.[10-13]

In conclusion, we have demonstrated for the first time the formation of a new fullerene family with a radioactive metal atom inside the cage by neutron irradiation. The endohedral radioactive metallofullerenes were found to be as stable and separable as the usual normal endohedral metal complexes.

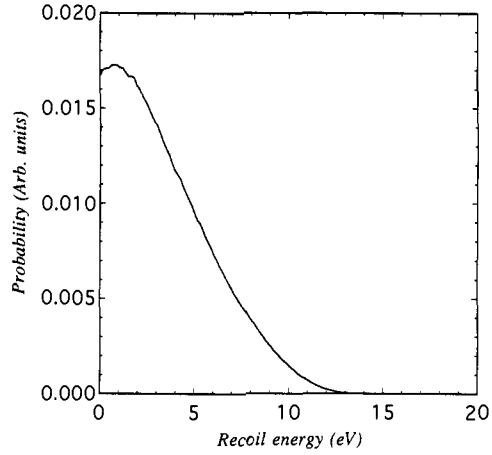

Figure 3. The recoil energy distribution associated with the β decay of the nuclear reaction $^{161}Gd \rightarrow {}^{161}Tb$. Nuclear data on β decay were taken from ref 9.

Furthermore, considering the potential ability endowed by the ultrahigh sensitivity of detection of radioactive species and the endohedral form of metallofullerenes, the encapsulated-radioactive-atom fullerene would open novel research fields not only as a new type of a carrier for a radioactive source[14] but also as a molecular tracer with a definite size and shape.

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(10) Galdwell, K. A.; Giblin, D. E.; Gross, M. L. *J. Am. Chem. Soc.* **1992**, *114*, 3743.
(11) Christian, J. F.; Wan, Z.; Anderson, S. L. *J. Phys. Chem.* **1992**, *96*, 3574.
(12) Wurz, P.; Lykke, K. R. *J. Phys. Chem.* **1992**, *96*, 10129.
(13) O'Brien, S. C.; Heath, J. R.; Curl, R. F.; Smalley, R. E. *J. Chem. Phys.* **1988**, *88*, 220.
(14) Mackey, D. W. J.; Burch, W. M.; Dance, I. G.; Fisher, K. J.; Willett, G. D. *Nucl. Med. Commun.* **1994**, *15*, 430.