

Formation of Po@C₆₀

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Radioactive endohedral fullerenes, ²¹⁰Po@C₆₀ and the dimers, are detected by using radiochemical and radiochromatographic techniques. The results show that a Po atom can be inserted into C₆₀ by a recoil process following a nuclear reaction. Using *ab initio* molecular dynamics simulations based on the all-electron mixed-basis approach, we also theoretically showed that the formation of a Po doped fullerene is possible. These findings may be useful for several nuclear applications such as nuclear medicine and/or nuclear waste disposal.

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Endohedral fullerenes which have atoms inside the C₆₀ cage have attracted great current interest in the physical and/or chemical properties. However, the production rate of the endohedral C₆₀ is quite low compared to the ordinary C₆₀. For pre-existing C₆₀, Saunders *et al.*^{1,2} have demonstrated the possibility of incorporating noble-gas atoms into fullerenes under high-pressure and high-temperature conditions. Braun *et al.*, Gadd *et al.*, and Sahoo *et al.*³⁻⁶ have produced an atom-doped C₆₀ by using the prompt-gamma or particle recoil induced by neutron irradiation. However, only partial information on the formation process, on the produced materials, and on the nature of the chemical interaction between a foreign atom and a fullerene cage have been established.

So far, we examined the production of fullerene derivatives created when alkali, alkali-earth, transition metals, 3B-6B elements and noble-gas elements, were produced by nuclear reactions induced by irradiation of samples with high-energy bremsstrahlung or charged particles. We found that the radioactive Be,⁷ C,⁸ N, noble-gas elements,⁹ and 3B-6B (Refs. 10 and 11) elements can be doped in fullerenes. In contrast alkali, alkali-earth and transitional metals do not remain in the fullerene portion.¹⁰

Such radioactive fullerenes and their derivatives are of considerable interest not only for following the location and metabolism of these substances in living organisms¹²⁻¹⁸ but also for nuclear waste disposal applications where the fullerene may serve as a nano-container of radioactivities.¹⁹

Here, we show that even a heavy nuclide like the ²¹⁰Po isotope can be inserted into C₆₀ from outside of the cage by nuclear recoil. In order to theoretically check the possibility of direct insertion, we carried out *ab initio* molecular-dynamics (MD) simulations based on the all-electron mixed-basis approach. We have newly implemented in our program the AO's with the extended *f*-electron symmetry including a semi-relativistic effect in order to treat the Po atom. We found that the results of MD simulations are consistent with the experimental results for the Po atom.

To produce the source of radioactive nuclides, Bi₂O₃ was used in powder form. The grain size of the materials was smaller than 100 meshes (20 μm). Purified fullerene (C₆₀) was carefully mixed with each material (weight ratio=1:1)

in an agate mortar, adding a few ml of carbon disulfide (CS₂). After drying up, about 100 mg of the mixture sample was wrapped in a pure aluminum foil of 10 μm in thickness for irradiation. Irradiation with 16 MeV deuterons was performed at the Cyclotron Radio-Isotope Center, Tohoku University. The beam current was typically 1 μA and the irradiation time was about 5 h. Only ²¹⁰Po (α -source) can be produced in the ²⁰⁹Bi(*d,n*) reaction. The radionuclide produced, its characteristic α -ray, its half-life, and the nuclear reaction are 5.3 MeV, 139 days and ²⁰⁹Bi(*d,n*)²¹⁰Po, respectively. The sample was dissolved in CS₂ and filtered through a millipore filter (pore size=0.2 μm) to remove insoluble materials. The soluble portion was injected into a HPLC device equipped with a 5PBB (Cosmosil) at a flow rate of 3 ml/min. For the confirmation of fullerenes and their derivatives, an UV detector was installed with a wavelength of 400 nm. In order to measure the α -rays emanating from ²¹⁰Po, eluent fractions were collected for 30 s intervals. After drying up the CS₂ solvent on a stainless-steel plate, the 5.3 MeV α -ray activities from ²¹⁰Po of each fraction were measured in a vacuum chamber with a silicon surface-barrier detector (SSD) coupled to a 1024-channel pulse-height analyzer. Therefore, radioactive ²¹⁰Po could be uniquely detected by means of its characteristic α -rays.

Figure 1 shows for materials inserted into C₆₀ samples, a radiochromatogram measured with an α -detector and a chromatogram measured with an UV detector, both plotted versus retention time after injection. A clear correlation between the UV-absorption intensity and the α counting rate in the 6.5–7 min interval is seen in Fig. 1. From the correlation of the elution behavior between the UV chromatogram and the radioactivities of the ²¹⁰Po atoms, we found that the atom-doped fullerene ²¹⁰PoC₆₀ was indeed produced by nuclear recoil implantation.

Such a clear correlation between the elution behavior of the C₆₀ populations and the radionuclide populations indicates that the radioactive ²¹⁰Po may become encapsulated inside the C₆₀ cages, even if the ion radius is greater than that of five- or six-membered rings. In order to theoretically check the possibility of direct insertion, we turn our attention to the *ab initio* molecular dynamics simulations. The method

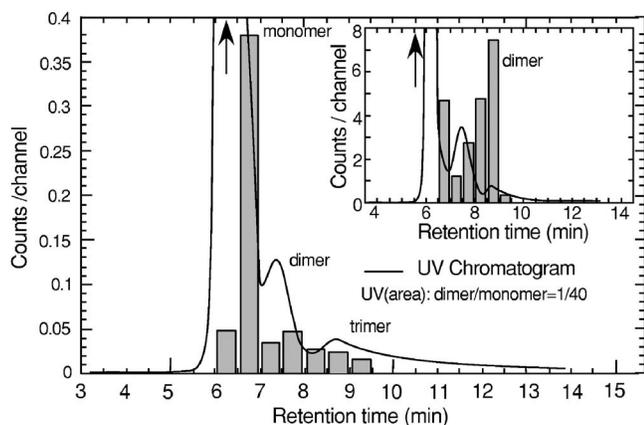


FIG. 1. HPLC elution behavior of the soluble portion of the crude extracted in the deuteron irradiated sample of $C_{60}+Bi_2O_3$. Plotted versus the retention time along the horizontal axis is a histogram of the α counting rate (in counts/s) measured with a solid-state Si-detector and a solid curve representing a chromatogram measured with an UV detector. (The inserted figure is for three-times-extraction in CS_2 using an ultrasonic apparatus.)

used here is based on the all-electron mixed basis approach^{7,21} using both plane waves (PW's) and atomic orbitals (AO's) as a basis set within the framework of the local density approximation (LDA) in density functional theory. For the LDA exchange-correlation function, we adopt Ceperley-Alder's fitting form. In the present study, we have recently implemented in our program the AO's with the f symmetry including a semi-relativistic effect in order to treat the Po atom. To generate the f AO's as well as the s , p and d AO's defined inside the non-overlapping atomic spheres, we use an atomic program based on Herman-Skillman's framework with logarithmic radial meshes. We use a supercell composed of $64 \times 64 \times 64$ meshes (with a mesh corresponding to 0.196 Å), in which we put one C_{60} molecule and one Po atom at a distance 1.50 Å outside from the center of a six-membered ring of C_{60} . For the present system, we use 339 AO's and 4169 PW's corresponding to a 7 Ry cutoff energy. For dynamics, we use an adiabatic approximation, and set the basic time step as $\Delta t=0.1$ fs and perform five steepest descent (SD) iterations after each update of atomic positions. The Po atom has a given initial velocity toward the center of the six-membered ring of C_{60} . We do not impose any velocity control, so that the system is almost microcanonical with little energy dissipation from the SD algorithm.

Figure 2 represents several snapshots of our simulation where Po hits the center of the topmost six-membered ring with the 40 eV initial kinetic energy. It is very surprising that such large atoms as Po can be so easily encapsulated from the outside. When Po approaches the six carbon atoms forming the topmost six-membered ring, these carbon atoms are pushed down. Simultaneously, Po enlarges the hole of this six-membered ring and goes through it. When the Po atom penetrates inside the C_{60} cage, the topmost six carbon atoms are lifted up from the lower carbon atoms and continue to oscillate for some time. Thus we find that Po is successfully encapsulated and $Po@C_{60}$ is created.

To check the amount of $^{210}Po@C_{60}$ produced, we per-

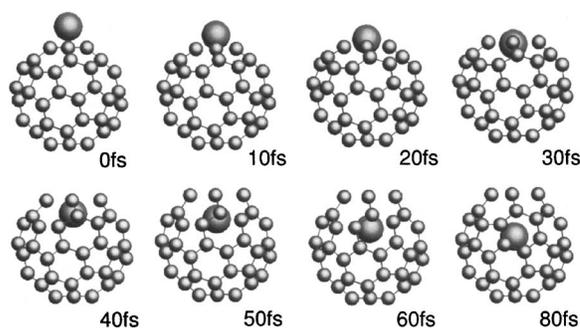


FIG. 2. Simulation of Po hitting the center of a six-membered ring of C_{60} with a kinetic energy of 40 eV. Here, the local skeleton disappears from the figure when the bond-length is elongated by more than 1.5 Å.

formed three times extractions in CS_2 solvent using an ultrasonic generator for the sample irradiated. The result of the α -spectrometry in each fraction is shown in the inserted figure in Fig. 1. Even though there is a slight delay in the chromatogram, populations of ^{210}Po were seen in the 6.5–7 min and 8–9 min intervals. It was found that the amounts of the soluble materials extracted in the three-times extraction were about twenty times greater than in the one-time extractions in the CS_2 solvent. The observation of the second peak (8–9 min) corroborates the formation of endohedral fullerene dimers with encapsulated radionuclides, namely $^{210}Po@C_{60}-C_{60}$. It seems that the shock of the collisions produces fullerene dimers through interactions with a neighboring fullerene cage.

For further characterization of the components in these peaks observed by the UV, the fraction corresponding to the second peaks in Fig. 1 were collected and examined with a TOF mass spectrometry. This result exhibits a series of peaks at $m/z1440-24n$ ($n=1, 2, \dots$) corresponding to the molecular ion peak of $C_{120-n}C_2$. The appearance of these fragmented peaks is characteristic of the mass spectrum of the C_{120} molecule.²⁰ However, the amount of endohedral fullerenes included such radioactivities is estimated to be about 10^{10} molecules, therefore, it may be difficult to detect such $^{210}Po@C_{60}$ molecules by a mass spectrometry.

In the present study, radioactive nuclides are produced by (d, n) reactions. The energetic nuclides should destroy the fullerene cages because the K.E. is estimated to be of a quite different order of magnitude than the energies (eVs) of molecular bonding. Therefore, the atoms being produced escape from their own material due to the K.E. of about a few hundred kiloelectron volts. Then, the kinetic energies are reduced in the sample to a magnitude which is appropriate for the fusion. Finally, the radionuclides hit the C_{60} cages and stop in the cage (formation of endohedral fullerene) and, furthermore, the shock produces fullerene polymers by interaction with a neighboring fullerene cage.

Such endohedral fullerenes can serve as a nano-containers of radioactivities and deliver them to the objective tissues in various metabolic pathways. Here, $^{210}Po@C_{60}$ molecules can be easily broken to pieces due to the energy release of α -ray (5.3 MeV) from ^{210}Po and that from the residual nuclide (^{206}Pb , a few hundred keV). And, the α -ray may attack

H																	He				
Li	Be ^s															B	C ^s	N ^s	O	F	Ne
Na ^s	Mg															Al	Si	P	S	Cl	Ar
K	Ca ^s	Sc ^s	Ti	V ^s	Cr ^s	Mn ^s	Fe	Co ^s	Ni ^s	Cu	Zn ^s	Ga ^s	Ge ^s	As ^s	Se ^s	Br	Kr ^s				
Rb	Sr	Y	Zr	Nb ^s	Mo ^s	Tc ^s	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb ^s	Te ^s	I	Xe ^s				
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po ^s	At	Rn				

FIG. 3. Schematic view of a Periodic Table. In the figure, a symbol (section) indicates the elements investigated in the present work. The formation of foreign-atom-doped fullerenes (C_{60}) can be possible in the elements shown by the dark box.

the objective tissues in the body following the explosion of the nano-container (C_{60}). Furthermore, if the complex isotopes ^{207}Po (positron emitter) and ^{210}Po and/or ^{206}Po (α emitter) are used, it can be followed the metabolic pathway by the annihilation gamma-rays with a positron emission tomography (PET). Therefore, if a suitable preparative technique could be developed, there may be valuable applications of these in nuclear medicine and/or as tracers. Recent advances in fullerene chemistry may also make it possible to control fullerene absorption/excretion profiles in the future.

Finally, several elements in a periodic table have been investigated by a recoil implantation following nuclear reactions. A schematic view of a Periodic Table is shown in Fig.

3. Here, elements shown by the symbol (section) are investigated by the present method. In the figure elements, which are experimentally confirmed to combine with fullerene cages, are shown in the dark area. It is interesting to note that the group elements such as 4B-6B and noble-gas might possibly form complex materials. Further, it is suppressed that Po is successfully encapsulated to create $\text{Po}@C_{60}$ even in such heavier nuclide.

In this study, the formation of ^{210}Po doped fullerenes has been investigated by using nuclear reactions. It was found that the Po atoms remained in the C_{60} portion after a HPLC process. This fact suggests that the formation of endohedral fullerenes is possible by a recoil process following nuclear reactions, even if the ion radius is greater than that of five- or six-membered rings. By carrying out *ab initio* molecular-dynamics (MD) simulations on the basis of the all-electron mixed-basis approach, we theoretically supported that the insertion of the Po atom into C_{60} through five- or six-membered rings is possible.

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- ¹M. Saunders, R. J. Cross, H. A. Jimenez-Vazquez, R. Shimshi, and A. Khong, *Science* **271**, 1693 (1996).
- ²A. Khong, R. J. Cross, and M. Saunders, *J. Phys. Chem. A* **104**, 3940 (2000).
- ³T. Braun and H. Rausch, *Chem. Phys. Lett.* **288**, 179 (1998).
- ⁴T. Braun and H. Rausch, *J. Radioanal. Nucl. Chem.* **243**, 27 (2000).
- ⁵G. E. Gadd, P. J. Evans, D. J. Hurwood, P. L. Morgan, S. Moricca, N. Webb, J. Holmes, G. McOrist, T. Wall, M. Blackford, D. Cassidy, M. Elcombe, J. T. Noorman, P. Johnson, and P. Prasad, *Chem. Phys. Lett.* **279**, 108 (1997).
- ⁶R. R. Sahoo, A. D. Bokare, and A. Patnaik, *Carbon* **40**, 2453 (2002).
- ⁷T. Ohtsuki, K. Masumoto, K. Ohno, Y. Maruyama, Y. Kawazoe, K. Sueki, and K. Kikuchi, *Phys. Rev. Lett.* **77**, 3522 (1996); T. Ohtsuki, H. Yuki, M. Muto, J. Kasagi, and K. Ohno, *ibid.* **93**, 112501 (2004).
- ⁸T. Ohtsuki, K. Masumoto, K. Sueki, K. Kobayashi, and K. Kikuchi, *J. Am. Chem. Soc.* **117**, 12869 (1995).
- ⁹T. Ohtsuki, K. Ohno, K. Shiga, Y. Kawazoe, Y. Maruyama, and K. Masumoto, *Phys. Rev. Lett.* **81**, 967 (1998).
- ¹⁰T. Ohtsuki, K. Ohno, K. Shiga, Y. Kawazoe, Y. Maruyama, and K. Masumoto, *J. Chem. Phys.* **112**, 2834 (2000).
- ¹¹T. Ohtsuki, K. Ohno, K. Shiga, Y. Kawazoe, Y. Maruyama, and K. Masumoto, *Phys. Rev. B* **60**, 1531 (1999); T. Ohtsuki, K.

- Ohno, K. Shiga, Y. Kawazoe, Y. Maruyama, K. Shikano, and K. Masumoto, *ibid.* **64**, 125402 (2001); T. Ohtsuki, K. Ohno, K. Shiga, Y. Kawazoe, and H. Yuki, *ibid.* **65**, 073402 (2002).
- ¹²S. H. Friedman, D. L. Decamp, R. P. Sijbesma, G. Srdanov, F. Dudl, and G. L. Kenyon, *J. Am. Chem. Soc.* **115**, 6506 (1993).
- ¹³S. H. Friedman, P. S. Ganapathi, Y. Rubin, and G. L. Kenyon, *J. Med. Chem.* **41**, 2424 (1998).
- ¹⁴T. Braun, *J. Radioanal. Nucl. Chem.* **259**, 331 (2004).
- ¹⁵S. Yamago, H. Tokuyama, E. Nakamura, K. Kikuchi, S. Kananishi, K. Sueki, H. Nakahara, S. Enomoto, and F. Ambe, *Chem. Biol.* **2**, 385 (1995).
- ¹⁶W. J. Anton, R. W. Stephen, and I. S. David, *Bioorg Med. Chem.* **4**, 767 (1996).
- ¹⁷L. J. Wilson, D. W. Cagle, T. P. Thrash, S. J. Kennel, S. Mirzadeh, J. M. Alford, and G. J. Ehrhardt, *Coord. Chem. Rev.* **192**, 199 (1999).
- ¹⁸T. P. Thrash, D. W. Cagle, J. M. Alford, K. Wright, G. J. Ehrhardt, S. Mirzadeh, and L. J. Wilson, *Chem. Phys. Lett.* **308**, 329 (1999).
- ¹⁹I. Amato, *Science* **258**, 1886 (1992).
- ²⁰T. Ohtsuki, K. Masumoto, T. Tanaka, and K. Komatsu, *Chem. Phys. Lett.* **300**, 661 (1999).
- ²¹K. Ohno, F. Mauri, and S. G. Louie, *Phys. Rev. B* **56**, 1009 (1997).