Isolation and Characterization of Light Actinide Metallofullerenes

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The fullerenes encapsulating metal atoms, called metallofullerenes, are extremely interesting materials with their properties originating from the interplay of the endohedral atoms with the carbon cage of various sizes and configurations. The first synthesis of actinide fullerenes was reported by Guo et al.,[1] who prepared uranium fullerenes and observed UC_{28} and UC_{60} in the primary soot. The second trial[2] was made by Diener et al., who found UC_{60}, UC_{82}, etc. in the sublimed soot. From the XPS study of the gross products reported in the former paper, the authors concluded that the uranium atom encapsulated in the C_{2n} carbon cage was in the +4 valence state. But observed data were merely reflecting bulk property, not the property of the individual molecule. Recently, it was reported that the valence state of metal atoms is sometimes changed by the surrounding carbon cage or by the number of encapsulated atoms.[3] It is important from the viewpoint of inorganic chemistry and fullerene sciences to reveal the properties of isolated metallofullerene molecules. From our knowledge of inorganic chemistry, it is generally known that the most stable valence state of uranium is +6 while it is +4 in the aerobic atmosphere and in a more reducing atmosphere it becomes +3. In this work, we report the production of metallofullerenes for U, Np, and Am and identification of uranium metallofullerene species. The soot containing actinide metallofullerenes was prepared by the arc-discharge method[4,5] by using a carbon rod which contained lanthanum as a carrier (with the number of atoms ratio of 100/1 for C/La) and radioactive tracers of ^{237}U, ^{239}Np, and ^{240}Am produced at the TANDEM accelerator of JAERI. The crude metallofullerenes were extracted by CS_2 and then redissolved in toluene for injection into HPLC columns of Buckyprep and 5PBB. Elution from columns was performed with toluene as the developing solvent and the eluate was monitored on-line by a UV detector and off-line by X- or γ-ray measurements. A macroscopic quantity of uranium fullerenes was prepared by the same method except for using ^{238}U carrier instead of the La carrier in the carbon rod with the atomic ratio of 100/1 for C/U. The uranium fullerene products were isolated by a 2-step HPLC column separation using a Buckyprep column preceded by the 5PBB. Two kinds of isolated uranium-containing fullerenes were identified by TOF/MS measurements for their mass and the purity of the isolation. The yields for production of metal-containing fullerenes were determined from the amount of radioactivity found in the extracted crude product relative to that initially present in the primary soot. The yields of light actinide fullerenes were found to be about 1.4 to 3.6 times larger than those of lanthanide-containing fullerenes. This result is in agreement with that reported by Diener et al. for uranium,[2] although the production conditions were completely different. Figure 1a,b shows the results of HPLC elutions of the actinide fullerenes using radiotracers with the Buckyprep column (panel a) and 5PBB column (panel b). In both figures, the elution behaviors of U, Np, and Am fullerenes were found extremely similar to that of Ce fullerenes (Ce was present as a contaminant from fission products in the sample of radiotracers), with the largest elution peak at the retention time known for $M@C_{82}$ of trivalent lanthanides.[6] In the experiment using the rod containing a macroscopic amount of U, two kinds of uranium fullerene species were found as the major products and they were purified by the 2-step column separation using a 5PBB column followed by a Buckyprep column. The result is shown in Figure 2. The species were identified to be $U@C_{82}$ (see insert in Figure 2) and $U_2@C_{80}$ by TOF/MS measurements, and the purity of the former fraction was estimated to be about 95%. It is interesting to note here that formation of $M_2@C_{80}$ species has been observed

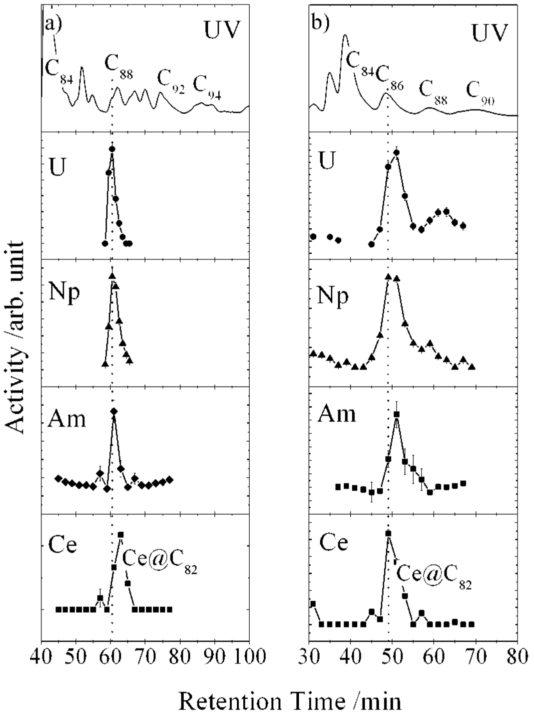

Figure 1. HPLC elution behavior of light actinide fullerenes. (a) The HPLC elution curve for the Buckyprep column (the size of this column is 10 ϕ mm × 250 mm, Nakalai Tesque Inc.) with a 3 mL injection volume and elution with toluene at 3.2 mL/min. The major elution peaks of U, Np, and Am are observed at the retention time of around 60 min, which corresponds to the retention time of $Ce@C_{82}$. (b) The HPLC elution curve for the 5PBB column (the size of this column is 10 ϕ mm × 250 mm, Nakalai Tesque Inc.) with a 3 mL injection volume and elution by toluene at 6 mL/min. The major elution peaks of U, Np, and Am are observed at the retention time of around 50 min in agreement wih the retention time for $Ce@C_{82}$.

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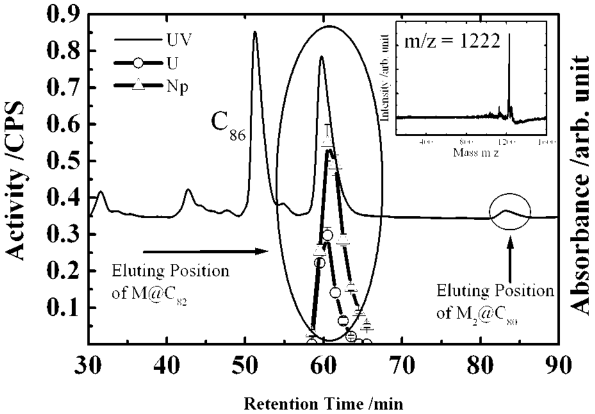

Figure 2. HPLC elution curve for the 2nd step column separation. In the first step separation, a 5PBB column was used with toluene as the developing solvent at the flow rate of 6 mL/min. The C_{86} fraction (around 50 min) was collected and then injected into a Buckyprep column with flow rate of 3.2 mL/min. The insert at the upper right is the mass spectrum of M@C_{82} (around 60 min) by using TOF/MS. The position of the elution peak for ^{239}Np is also shown by open triangles for comparison.

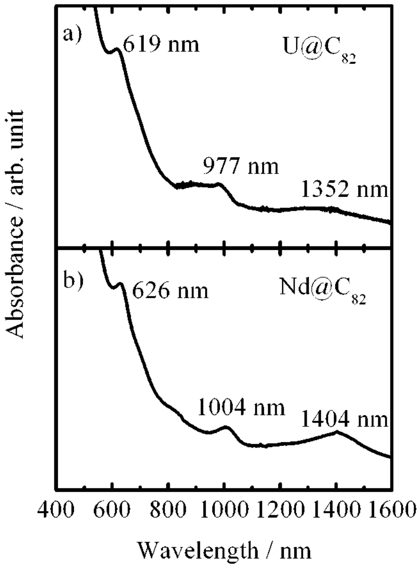

Figure 3. UV/vis/NIR absorption spectrum of U@C_{82}. (a) Absorption spectrum of U@C_{82} dissolved in toluene. Three characteristic absorption peaks are observed. (b) Absorption spectrum of Nd@C_{82} in toluene. The two absorption spectra are similar to three characteristic peaks but the peak positions are a little shifted to the smaller wavelengths in the spectrum of U@C_{82} compared to Nd@C_{82}.

only for the light lanthanide elements (La, Ce, Pr)[7−9] and this fact indicates that the affinity of uranium for formation of metallofullerenes is similar to that of light lanthanoids. In recent results, UV/vis/NIR absorption spectra of metallofullerenes have been shown to be generally sensitive to the metal oxidation state in metallofullerenes.[10−15] Figure 3 shows the UV/vis/NIR absorption spectrum of the isolated U@C_{82} in toluene. This spectrum has three characteristic absorption peaks at wavelengths 619, 977, and 1352 nm, almost the same as that of M@C_{82} of trivalent lanthanides.[10,11,16] To be more precise, the spectrum for U@C_{82} is most like that for Nd@C_{82} having a trivalent Nd with the f^3 electronic structure with two minor differences: one is the three absorption peaks are slightly and equally shifted for U@C_{82} to the higher energy side by 0.035 eV and the other is the intensity of the peak at 1352 nm is about half that of the peak at 1404 nm for Nd@C_{82}. Such similarity in the light absorption characteristics and the HPLC retention time strongly suggests that the oxidation state of the uranium atom in U@C_{82} is +3. It is to be added that no meaningful ESR signal was observed for the U@C_{82} sample dissolved in CS_2 similar to the behavior of Nd@C_{82}. Then, from the equivalence of the HPLC retention times and from similar 5f characterizations as actinide elements, it is reasonable to suggest that the major products for Np and Am fullerenes are also M@C_{82} species with the oxidation state of +3. In conclusion, two kinds of uranium metallofullerenes were produced by the conventional arc-discharge method by use of a carbon rod containing a macroscopic amount of uranium. They were separated by HPLC columns and identified as U@C_{82} and U_2@C_{80}. From the similarity of the photon absorption spectra among U@C_{82} and M@C_{82} for lanthanides, and from their HPLC behavior, it is concluded that the uranium atom in the C_{82} cage is in the +3 oxidation state. The experiments using carbon rods containing radiotracers of ^{237}U, ^{239}Np, and ^{240}Am with a macroscopic amount of lanthanum as a carrier gave Np and Am containing fullerenes that were eluted from the HPLC columns at the same retention time as for U@C_{82} and M@C_{82} (M = lanthanides). Similarity of the retention times for the Np and Am species suggests that the major products for Np and Am are also in the form of M@C_{82} with the metal atoms in the +3 oxidation state.

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