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Communications to the Editor

Production, Isolation, and Electronic Properties of Missing Fullerenes: $Ca@C_{72}$ and $Ca@C_{74}$

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There has been known to exist two "missing" fullerenes that have not yet been isolated in macroscopic amounts, i.e., C_{72} and C_{74}. The C_{72} and C_{74} fullerenes have a single IPR (isolated pentagon rule) structure, D_{6d} and D_{3h} symmetry structure for C_{72} and C_{74}, respectively.[1] So far the extraction of metallofullerenes[2] based on the missing fullerenes such as $Sc_2@C_{74}$[3,4] and $La_2@C_{72}$[5] has been reported. One of the salient electronic properties of the two missing fullerenes concerns their HOMO-LUMO gaps. C_{72} has a large HOMO-LUMO gap (1.388 eV),[6] which is larger than that of C_{70} (1.1 eV)[6] and comparable to that of C_{60} (1.6 eV). C_{72} has two hexagons which are completely surrounded by six hexagons. Although a simple Hückel MO calculation[7] suggests the stable D_{6d} structure for C_{72}, a more elaborate ab initio calculation[8] indicates that the presence of two such hexagons in the cage structure causes significant strain and thus produces a high structural instability. C_{74} has been observed in soot produced by arc discharge but has not yet been isolated. C_{74} has an unusually small HOMO-LUMO gap (0.224 eV),[6] suggesting a high chemical reactivity. This might explain the inability to extract C_{74} from primary soot by normal fullerene solvents.[9]

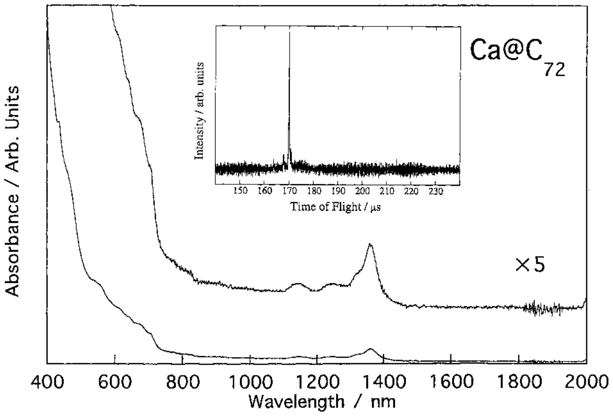

Figure 1. UV−vis−near-IR absorption spectrum of isolated $Ca@C_{72}$ in CS_2 solution. The insert shows a LD-TOF mass spectrum of the isolated $Ca@C_{72}$.

Here, we report the first successful production, separation, and isolation of endohedral calcium fullerenes with the two missing fullerene cages, C_{72} and C_{74}. Unlike the hollow C_{72} and C_{74}, we have found that $Ca@C_{72}$ and $Ca@C_{74}$ metallofullerenes are stable and even soluble in normal fullerene solvents and thus can be subjected to the normal HPLC purification. The calcium atoms obviously play crucial roles in stabilizing these missing cage-based matallofullerenes.

Soot containing $Ca@C_{72}$, $Ca@C_{74}$, and other calcium metallofullerenes ($Ca@C_{76}$ to $Ca@C_{100}$) was produced in direct-current (350−400 A) arc discharge of a calcium/graphite composite rod (Toyo Tanso Co. Ltd., 12.5 × 12.5 × 240 mm, 0.3 atomic %) under He flow (8−10 L/min) at 50 Torr. The soot was collected under totally anaerobic conditions[10−14] and extracted by CS_2. The $Ca@C_{72}$ and $Ca@C_{74}$ fullerenes were separated by the two-stage high-performance liquid chromatography (HPLC) method.[10−13] The retention time of $Ca@C_{72}$ was very close to those of C_{60} and C_{70} oxides, so that the final isolation of the $Ca@C_{72}$ was achieved by recycling (2−9 times) the HPLC process to increase the resolution.[15,16] Only a single isomer was found in both metallofullerenes, consistent with IPR for C_{72} and C_{74}. The relative yields of $Ca@C_{72}$ and $Ca@C_{74}$ are normally 0.5−1% of that of C_{60}.

Figure 1 shows a UV−vis absorption spectrum of the isolated $Ca@C_{72}$. The spectroscopic features are quite different from those of other calcium fullerenes such as $Ca@C_{82}$ (I−IV) and $Ca@C_{84}$ (I,II).[12] The onset of the absorption is 1500 nm, and several

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(15) In the first HPLC stage, the toluene solution of the extract was separated by a preparative recycling HPLC system (Japan Analytical Industry LC-908-C60) with a Cosmosil Buckyprep column (20 × 250 mm, Nacalai Tesque) with a typical flow rate of 18.0 mL/min. In the second stage with a Buckyclutcher I column (21 × 500 mm, Regis Chemical) with a flow rate of 9.30 mL/min, $Ca@C_{72}$ and $Ca@C_{74}$ were separated from other fullerenes. A semipreparative (10 × 250 mm) ODS column (Microsorb C18) was also used in the second stage.

(16) The mass number of $Ca@C_{72}$ (m/z 904) coincides with that of $C_{74}O$. However, the observed ^{13}C isotope distribution is almost exactly the same as that of the calculated distribution of $Ca@C_{72}$, which confirms the present isolation of the $Ca@C_{72}$ fullerene.

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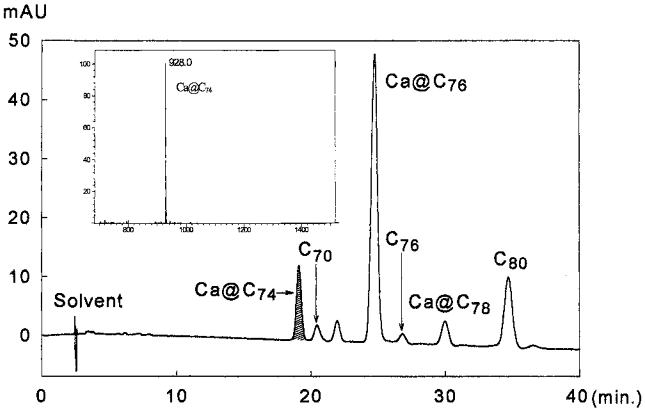

Figure 2. A second stage HPLC chromatogram of the $Ca@C_{74}$-containing fraction with a ODS column (4.6 mL/min; 313 nm detection; 55% toluene, 45% acetonitrile) collected by a Buckyprep HPLC in the first stage. The insert shows a negative DCI mass spectrum of the isolated $Ca@C_{74}$.

characteristic peaks are observed between 1200 and 1400 nm, suggesting an electron transfer from the calcium atom to the C_{72} cage.[10] The extremely low absorbance between 800 and 1100 nm is characteristic to $Ca@C_{72}$. $Ca@C_{74}$ has been similarly isolated by the two-stage HPLC protocol. Figure 2 shows a HPLC chromatogram of the fraction containing $Ca@C_{74}$ and $Ca@C_{76}$. The retention time of $Ca@C_{74}$ is unusually short as compared with other calcium fullerenes. This might be due to a highly symmetrical shape of $Ca@C_{74}$ with D_{3h} symmetry. A negative DCI mass spectrum of the purified $Ca@C_{74}$ is inserted in Figure 2, indicating the complete isolation of this species.

The present isolation of $Ca@C_{72}$ and $Ca@C_{74}$ indicates that even the unstable fullerene cages can be stabilized significantly upon encapsulation of a calcium atom. This is largely because that the endohedral doping causes the intra-fullerene electron transfers[17] from the calcium atom to the carbon cages, and thus alters the electronic structures near the HOMO-LUMO levels. The geometry-optimized structure of $Ca@C_{74}$ from an ab initio calculation is shown in Figure 3.[18] Almost two valence electrons on Ca ($4s^2$) are transferred to the LUMO of C_{74} forming a singlet electronic state, and the electronic structure is well described as $Ca^{2+}@C_{74}^{2-}$. As a result of the two-electron transfer from Ca to C_{74}, the HOMO and LUMO levels of $Ca@C_{74}$ become 0.99 eV lower and 1.7 eV higher than those of empty C_{74}, respectively. It is noticeable that the HOMO-LUMO gap of $Ca@C_{74}$ is 1.5 times as large as that of C_{74}. These suggest that $Ca@C_{74}$ becomes much less reactive than the empty C_{74}.

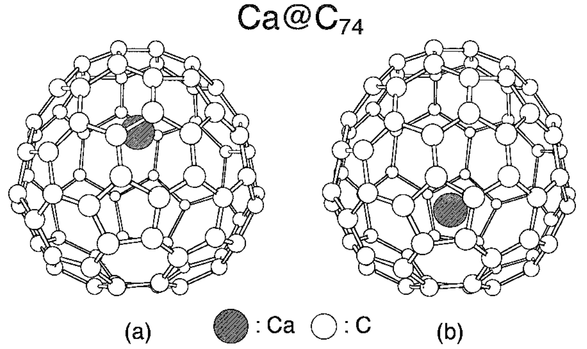

Figure 3. Optimized structures of $Ca@C_{74}$ by the present ab initio calculation. Strcuture **a** is 7 kcal/mol more stable than structure **b**. The Ca atom is along the symmetry axis. Since the calcium atom is not in the center, the symmetry of both structures decreases from D_{3h} to C_{2v}. The calculated nearest Ca−C distances are 2.802 and 2.824 Å for Figure 3, **a** and **b**, respectively.

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Supporting Information Available: Details of the HPLC separation and isolation of $Ca@C_{72}$ and $Ca@C_{74}$ (3 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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