Production and Isolation of $Ca@C_{82}$ (I−IV) and $Ca@C_{84}$ (I,II) Metallofullerenes

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Endohedral metallofullerenes are novel forms of fullerene materials and have gained wide interests in recent years.[1,2] Almost all of the metallofullerenes prepared so far have incorporated La,[1,3−5] Y,[6,7] and Sc[8−10] or several lanthanide elements such as Gd[11] and Pr.[12] The endohedral structures of $Y@C_{82}$ and $Sc_2@C_{84}$ have been finally confirmed by recent synchrotron X-ray powder diffraction[13] and ^{13}C NMR[14] studies, respectively. However, to date no report has been presented for production and isolation of the metallofullerenes involving other than the group IIIA and lanthanoid elements. Smalley and co-workers[15] and Kubozono et al.[16] have reported the production and solvent extraction of CaC_{60} and CaC_{70}. Unfortunately, the purification of these calcium fullerenes has not yet been performed. Here, we report the first production, isolation, and spectroscopic study on several structural isomers of $Ca@C_{82}$ and $Ca@C_{84}$.

The details of the production and separation/isolation of endohedral metallofullerenes have been described elsewhere.[14,17−19] Briefly, soot-containing $Ca@C_{82}$, $Ca@C_{84}$, and other calcium metallofullerenes 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[14,18,19] and was extracted by CS_2. The $Ca@C_{82}$ and $Ca@C_{84}$ fullerenes were separated and by the two-stage high-performance liquid chromatography (HPLC)[20,21] method.[14,17−20] The retention times of the present isomers are very close to each other, therefore the final isolation of the isomers was achieved by recycling (2−9 times) the HPLC process to increase the resolution.

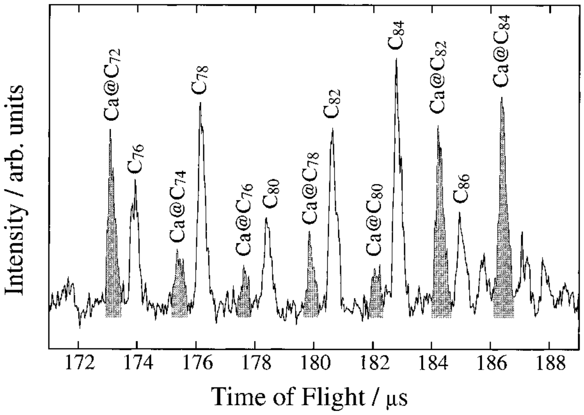

Figure 1. Laser-desorption (at 355 nm) TOF mass spectrum of a CS_2 extract of soot containing various $Ca@Cn$ ($72 \leq n$) fullerenes.

Figure 1 shows a laser-desorption time-of-flight (LD-TOF) mass spectrum of a carbon disulfide extract of the calcium fullerene containing soot. The $Ca@C_{72}$, $Ca@C_{82}$, and $Ca@C_{84}$ fullerenes are more abundant than the other calcium fullerenes. A calcium atom can be encapsulated within virtually all of the higher fullerenes. The mass spectrum shows the presence of a series of mono calcium fullerenes of $Ca@C_{72}$ to $Ca@C_{84}$. This is in strong contrast to the group IIIA and lanthanoid metallofullerenes so far reported,[1−9] where a metal atom has mainly been entrapped in C_{82}, except for scandium metallofullerenes ($Sc@Cn$ and $Sc_2@Cm$ ($74 \leq n$; $74 \leq m$).[8−10]

During an attempt to purify and isolate $Ca@C_{82}$ and $Ca@C_{84}$ by the two-stage HPLC method, we have noticed the presence of several structural isomers of these metallofullerenes. Hereafter, we call these isomers of the calcium fullerenes as isomer I, II, III, and so on in increasing order of retention time as we have used in $Sc_2@C_{84}$.[14] Notably, we have found four isomers (I−IV) of $Ca@C_{82}$ and two isomers (I, II) of $Ca@C_{84}$. An HPLC analysis (with a Buckyprep column) of the CS_2 extract reveals that $Ca@C_{82}$ isomers (I−IV) are found in the tail of a hollow C_{84} fraction, whereas $Ca@C_{84}$ isomers (I, II) are found in the onset of a C_{86} fraction. Panels a and b of Figure 2 show the HPLC chromatograms for the first and second HPLC stages, respectively, for the separation of $Ca@C_{82}$ (III) and $Ca@C_{82}$ (IV). As in Figure 2a, the retention times of the four isomers of $Ca@C_{82}$ are very close to each other under the present HPLC conditions. However, isomers III and IV of $Ca@C_{82}$, for example, can be separated and isolated in the second stage with a Buckyclutcher I column by recycling the corresponding HPLC

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(20) 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, $Ca@C_{82}$ (I−IV) and $Ca@C_{84}$ (I,II) were separated from hollow higher fullerenes.

(21) The retention times at 25 °C of isomers I, II, III, and IV of $Ca@C_{82}$ were 27.9, 28.4, 28.9 and 29.2 min on the Buckyprep column and 20.4, 20.4, 20.5, and 21.3 min on the Buckyclutcher column, respectively. The retention times of $Ca@C_{84}$ (I) and $Ca@C_{84}$ (II) were 30.7 and 30.7 min on the Buckyprep column and 20.6 and 20.9 min on the Buckyclutcher column at 25 °C, respectively.

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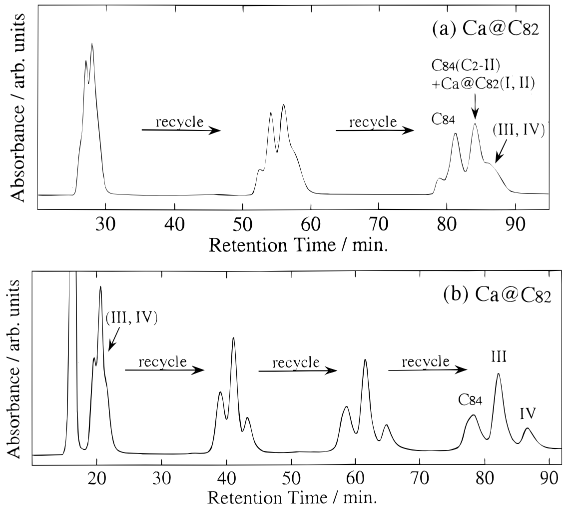

Figure 2. HPLC chromatograms of Ca@C_{82} (III) and (IV): (a) the first stage with a Buckyprep column and toluene eluent and (b) the second stage with a Buckyclutcher I column and toluene eluent.

fraction (Figure 2b). Isomers I and II of Ca@C_{82} and Ca@C_{84} can also be isolated by similar two-stage HPLC procedures with 2−9 recycles of the fractions. The purity of these calcium metallofullerenes relative to other fullerenes was greater than 99.0%.

UV-vis-near IR absorption spectra of the present calcium fullerenes are also quite different from those of the group IIIA and lanthanoid metallofullerenes such as La@C_{82}, Y@C_{82}, and Gd@C_{82}. Figure 3a,b give the absorption onsets of Ca@C_{82} (I−IV) and Ca@C_{84} (I, II), respectively, in the vis-near IR regions. Several distinct features of the spectra are readily discernible: (1) two distinct absorption onsets are observed at around 1200 nm (for Ca@C_{82} (II, III) and Ca@C_{84} (I, II)) and 1800 nm (for Ca@C_{82} (I, IV)); (2) the absorption features of the present calcium fullerenes are much more salient and highly structured than those of the group IIIA and lanthanoid metallofullerenes (cf., Figure 3c); (3) the spectral features of Ca@C_{84} (I) and (II) are similar to each other.

The spectral difference can be ascribed to the intrafullerene electron transfers from encaged metal atoms to the corresponding carbon cages. It is well-known that the formal electronic structures of La@C_{82} and Y@C_{82} are well-represented by La^{3+}@C_{82}^{3-} [4,22] and Y^{3+}@C_{82}^{3-},[6,7,22] respectively, whereas a very recent theoretical calculation[23] indicates that the oxidation state of Ca@C_{82} is Ca^{2+} instead of Ca^{3+}. Furthermore, our attempts to observe ESR hyperfine splitting for the present calcium fullerenes have not been successful either at room temperature or at low temperature, indicating that the isomers of Ca@C_{82} and Ca@C_{84} are diamagnetic (ESR-silent) in contrast to the paramagnetic behavior of Sc@C_{82},[8,10] Y@C_{82},[6,7] and La@C_{82}.[4] Therefore, it is highly probable that all of the encaged metal atoms of the present isomers of Ca@C_{82} and Ca@C_{84} have the oxidation states of +2.

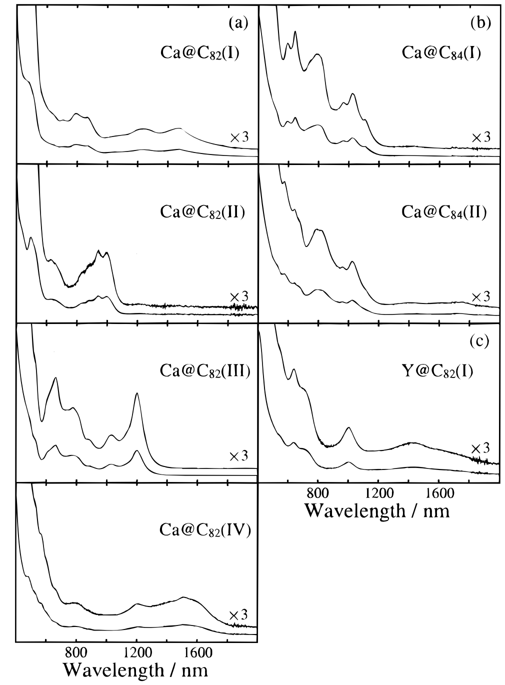

Figure 3. UV-vis-near IR absorption spectra of (a) Ca@C_{82} (I−IV), (b) Ca@C_{82} (I, II), and (c) Y@C_{82} (I) for comparison.

The paramagnetic character of M@C_{82} (M = Sc, Y, La) has precluded ^{13}C NMR determination of the isomer structures. The diamagnetic character of the present calcium fullerenes, on the other hand, enables us to determine the symmetry of the isomers. Detailed ^{13}C NMR studies on Ca@C_{82} (III) and Ca@C_{84} (I) are now in progress.

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