Isolation and Characterization of a New Isomer of $Ca@C_{72}$

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(Received April 8, 2004; CL-040385)

We isolated a new (second) isomer of $Ca@C_{72}$. As a result of this discovery, it was confirmed that at least one of the two $Ca@C_{72}$ isomers has a C_{72} cage that does not satisfy the so-called isolated pentagon rule (IPR), because C_{72} has only one IPR cage structure.

In general, fullerenes are composed of pentagonal and hexagonal rings. The isolated pentagon rule (IPR), which states that all pentagons should be isolated in stable fullerenes, has been a very important empirical rule for unraveling the structures of fullerenes.[1] However, IPR-violating metallofullerenes have recently been reported, including $Sc_2@C_{66}$,[2] $Sc_3N@C_{68}$,[3] and $La_2@C_{72}$.[4] Two or more metal atoms are encapsulated in these IPR-violating metallofullerenes, and electron transfer from the encaged metal atoms to the cage has been thought to stabilize unstable fused pentagons. In this context, it has been an interesting question to determine whether or not IPR-violating metallofullerenes containing a single metal atom inside the cage exist.

In 1998, Wan et al. reported the isolation of a single isomer of $Ca@C_{72}$.[5] Theoretical calculations of $Ca@C_{72}$ predicted that it has a non-IPR cage structure,[6] but the cage structure of $Ca@C_{72}$ has never been elucidated experimentally. Here, we report the isolation of a new (second) isomer of $Ca@C_{72}$. This finding indicates that at least one of the two isomers of $Ca@C_{72}$ has a non-IPR cage structure, i.e., $Ca@C_{72}$ is the first-known IPR-violating metallofullerene with a single metal atom.

Soot containing $Ca@C_{72}$ was produced by direct current (40 A) arc discharge of Ca/C composite rods under a 500 Torr He atmosphere. Both empty fullerenes and metallofullerenes were extracted from the raw soot by refluxing with 1,2,4-trichlorobenzene for 6 h. The isolation of two different isomers, $Ca@C_{72}$(I) and $Ca@C_{72}$(II), was accomplished by three-stage high-performance liquid chromatography (HPLC), where $Ca@C_{72}$(I) is the isomer reported by Wan et al. and $Ca@C_{72}$(II) is the new variant. The purity of the isolated species was confirmed by laser-desorption time-of-flight mass spectrometry. The UV–vis–NIR absorption spectra of the two isomers were measured in CS_2 solution.

Details of the purification and isolation of the two $Ca@C_{72}$ isomers are as follows. In the first HPLC stage (Figure 1a), we roughly separated $Ca@C_{72}$ by using two COSMOSIL 5PBB columns (20 × 250 mm, Nacalai Tesque; 6 mL/min flow rate; CS_2 eluent). $Ca@C_{72}$(I) was eluted with C_{70}, and $Ca@C_{72}$(II) with C_{76} and C_{78}. Further separation of $Ca@C_{72}$(I) was carried out by twice using a COSMOSIL Buckyprep column (20 × 250 mm, Nacalai Tesque; 12 mL/min flow rate; toluene eluent) (Figure 1b and 1c). In the second stage for $Ca@C_{72}$(II) (Figure 1d), a COSMOSIL Buckyprep column (20 × 250 mm, Nacalai Tesque; 12 mL/min flow rate; toluene eluent) was used to collect the fraction containing $Ca@C_{72}$(II) with C_{76}. Finally, in the third stage (Figure 1e), the isolation of $Ca@C_{72}$(II) from C_{76} was achieved using a COSMOSIL 5PBB column (20 × 250 mm, Nacalai Tesque; 12 mL/min flow rate; toluene eluent). However, as mentioned later, the purified $Ca@C_{72}$(II) was found to contain a trace amount of $Ca@C_{72}$(I). The yields of the two $Ca@C_{72}$ isomers were considered to be almost the same, and were much lower than that of $Ca@C_{82}$, which is the most widely investigated Ca-metallofullerene.

The HPLC profile of the mixture of two $Ca@C_{72}$ isomers on an analytical scale is shown in Figure 2. A COSMOSIL Buckyprep column (4.6 × 250 mm, Nacalai Tesque; 1 mL/min flow rate; toluene eluent) was used, and it confirms the difference in the retention times of the two isomers; the $Ca@C_{72}$(I) and $Ca@C_{72}$(II) were eluted at 18.5 and 19.9 min, respectively. Figure 3 shows the UV–vis–NIR absorption spectra of $Ca@C_{72}$(I) and $Ca@C_{72}$(II). The absorption spectrum of $Ca@C_{72}$(I) shows a peak at 1360 nm and is identical to that reported by Wan et al. On the other hand, the absorption spectrum

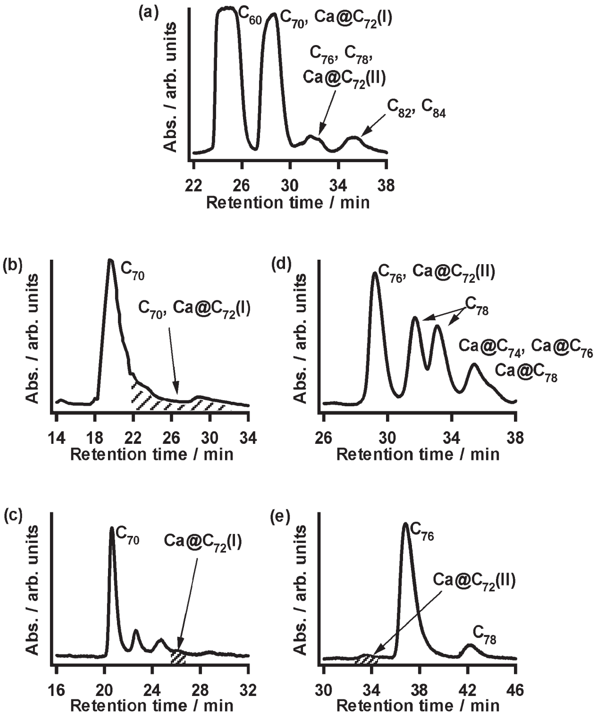

Figure 1. HPLC isolation scheme for $Ca@C_{72}$(I) and $Ca@C_{72}$(II). (a) The first stage with two COSMOSIL 5PBB columns. (b) The second stage for $Ca@C_{72}$(I) with a COSMOSIL Buckyprep column. (c) The third stage for $Ca@C_{72}$(I) with a COSMOSIL Buckyprep column. (d) The second stage for $Ca@C_{72}$(II) with a COSMOSIL Buckyprep column. (e) The third stage for $Ca@C_{72}$(II) with a COSMOSIL 5PBB column.

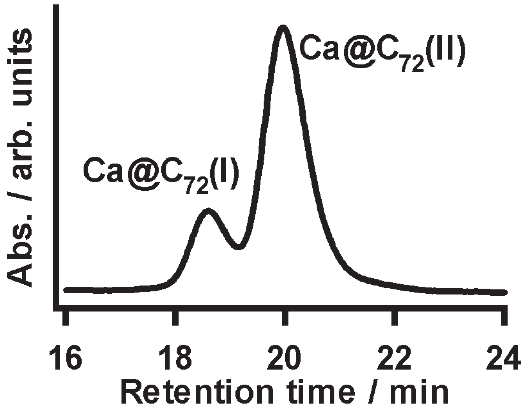

Figure 2. HPLC profile of the mixture of two Ca@C_{72} isomers on an analytical scale with a COSMOSIL Buckyprep column.

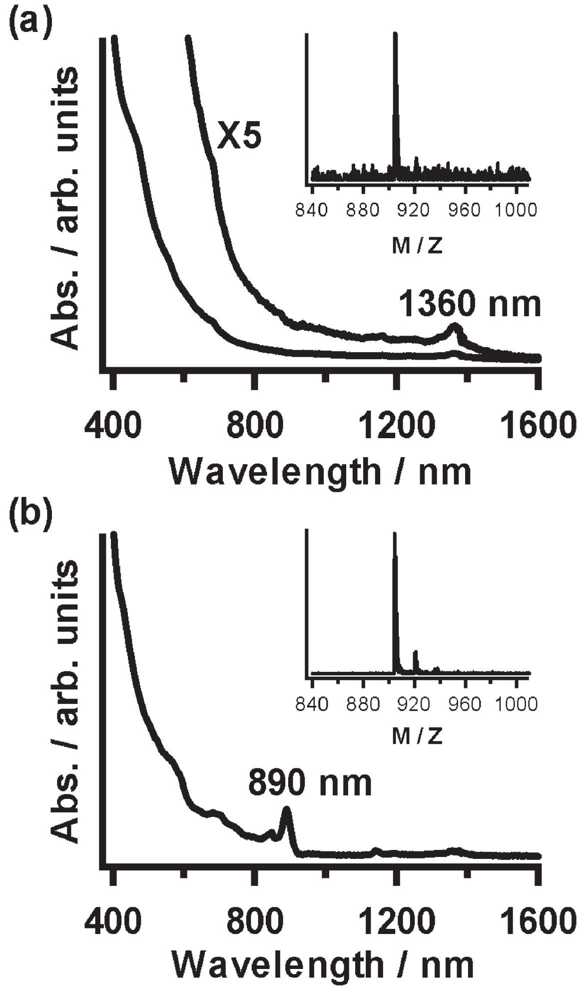

Figure 3. UV–vis–NIR absorption spectra of (a) Ca@C_{72}(I) and (b) Ca@C_{72}(II) in CS_2 solution at room temperature. The insets show positive LD-TOF mass spectra for the purified samples.

of Ca@C_{72}(II) has a notable peak at 890 nm and is obviously different from that of Ca@C_{72}(I). The small peak at 1360 nm can be attributed to Ca@C_{72}(I), which cannot be separated from Ca@C_{72}(II). The differences in the HPLC retention times and in the UV–vis–NIR absorption spectra between the two isomers can be attributed to their different cage structures. However, C_{72} has only one IPR cage structure. Therefore, we concluded that at least one of either Ca@C_{72}(I) or Ca@C_{72}(II) has a non-IPR C_{72} cage; in other words, it was shown that Ca@C_{72} is the first IPR-violating metallofullerene encapsulating a single metal atom. On the other hand, theoretical calculations[6] predicted that two Ca@C_{72} isomers with a non-IPR cage structure containing a pair of adjacent pentagons are more stable than an isomer with an IPR cage structure. Thus, it is likely that both of the Ca@C_{72} isomers that have been isolated have non-IPR cage structures. This prediction should be confirmed experimentally using a technique such as ^{13}C NMR spectroscopy.

T. K. and S. S. thank the Japanese Ministry of Education Culture, Sports, Science and Technology for Grants-in-Aid for Scientific Research (A)(1)(No. 13304026) for providing financial support for the present study.

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Published on the web (Advance View) July 12, 2004; DOI 10.1246/cl.2004.1008