Production and Characterization of Heteroatom-encapsulated Metallofullerene, CaHo@C_{82}

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We produced two CaHo@C_{82} isomers whose electronic states were characterized to be $Ca^{2+}Ho^{3+}@C_{82}^{5-}$ from the elution behavior of high-performance liquid chromatography.

In metallofullerenes, electron transfer from metal atom(s) to a carbon cage occurs and the valence of cage depends on inside metal species. For example, C_{82}-based metallofullerenes, which are the most widely investigated metallofullerenes,[1] show various electronic states[2–4] such as $Tm^{2+}@C_{82}^{2-}$, $La^{3+}@C_{82}^{3-}$, and $(Er^{3+})_2@C_{82}^{6-}$. However, metallofullerenes with C_{82}^{4-} and C_{82}^{5-} are missing.

Encapsulation of two heteroatoms with different valences is a promising way to generate the metallofullerenes whose cages have large odd number valences such as C_{82}^{5-} and C_{82}^{7-}. In our previous work,[5] we have synthesized the heteroatom-encapsulated metallofullerene, HoTm@C_{82}, because Ho and Tm were known to take trivalent and divalent in Ho@C_{82} and Tm@C_{82}, respectively.[2,6] Although HoTm@C_{82} was expected to possess a C_{82}^{5-} cage, the electronic state was elucidated to be $Ho^{3+}Tm^{3+}@C_{82}^{6-}$ by UV–vis–NIR absorption and X-ray absorption near edge structure. We speculated that this change of valence state for Tm should come from the large ionic radius of divalent Tm for encapsulation of two metal atoms inside the cage. In addition, it is important that Tm can take both divalent and trivalent state.[7] In this work, we have employed Ca instead of Tm, because Ca ion strongly prefers divalent state and its ionic radius is fairly small.

The soot containing CaHo@C_{82} was produced by direct current (450 A) arc discharge of calcium, holmium, and carbon composite rods under a He atmosphere of 400 Torr. The atomic ratio of Ca:Ho:C was 0.2:0.2:99.6. Both metallofullerenes and hollow fullerenes were extracted from the soot by refluxing with 1,2,4-trichlorobenzene for 8 h. Two CaHo@C_{82} isomers were isolated by multistep high-performance liquid chromatography (HPLC: Japan Analytical Industry Co. LC-908-C60). All the columns used in this work are made by Nacalai Tesque, and the column sizes are 20ϕ × 250 mm. Flow rates were 12 mL/min for toluene eluent and 6 mL/min for CS_2 eluent, respectively. The isolation of CaHo@C_{82} isomers were confirmed by laser-desorption time-of-flight mass spectroscopy (LD-TOF-MS: Bruker REFLEX II). The UV–vis–NIR absorption spectra of the two isomers were measured on a HITACHI U-3500 in CS_2.

Details of the purification and isolation of the two CaHo@C_{82} isomers are as follows. In the first step (Figure 1a), CaHo@C_{82} was roughly separated by using a COSMOSIL Buckyprep column with toluene eluent. Among the three types of possible dimetallofullerenes, CaHo@C_{82} and $Ho_2@C_{82}$ were found in the fractions depicted in Figure 1, but no $Ca_2@C_{82}$ was found in any fractions. In the second step (Figure 1b), serially connected two COSMOSIL 5PBB columns were used to eliminate the remaining hollow fullerenes such as C_{60}, C_{70}, and C_{88} from the fraction containing CaHo@C_{82} with CS_2 eluent, and CaHo@C_{82} was concentrated by recycling 12 times. Serially connected two COSMOSIL Buckyprep columns and a COSMOSIL 5PBB column were employed in the third and forth steps with toluene eluent, respectively. In the third step (Figure 1c), the fraction of CaHo@C_{82} was separated into two fractions of isomers I and II, both of which were independently subject to the forth step (Figures 1d and 1e). The fraction of isomer I was further purified by serially connected two COSMOSIL Buckyprep columns with toluene as a fifth step (not shown in Figure 1). On the other hand, the fraction of isomer II was directly submitted to the analysis.

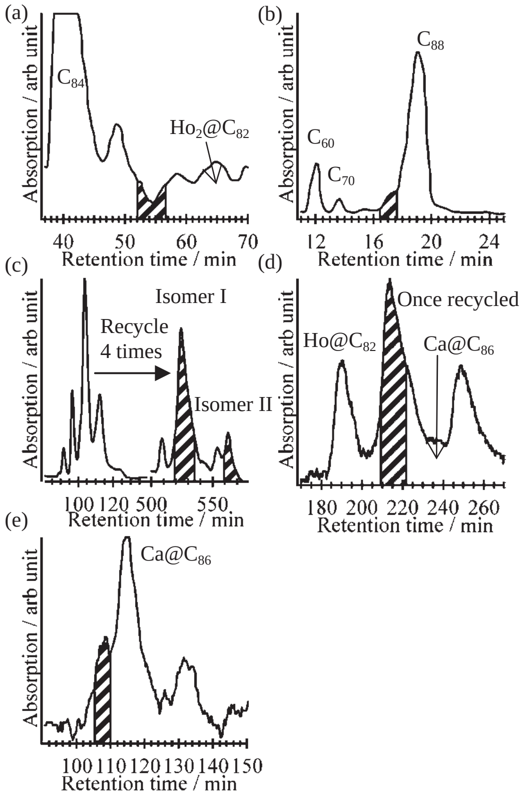

Figure 1. HPLC isolation profiles for CaHo@C_{82} (I) and CaHo@C_{82} (II). Fractions shaded in the profiles contain CaHo@C_{82}. (a) The first step with Buckyprep column. (b) The second step with two COSMOSIL 5PBB columns. (c) The third step with two COSMOSIL Buckyprep columns. (d) The forth step for CaHo@C_{82} (I) with a COSMOSIL 5PBB column The profile after recycling once is shown. (e) The forth step for CaHo@C_{82} (II) with a COSMOSIL 5PBB column.

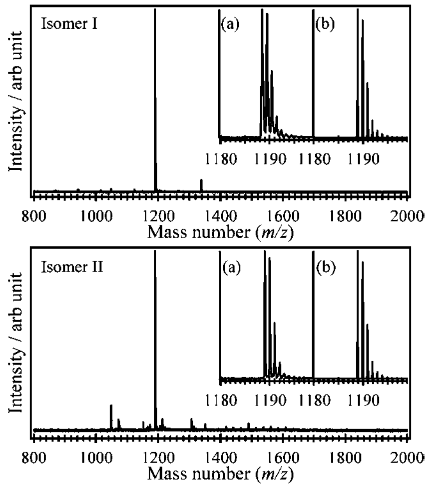

Figure 2. Mass spectra of two isomers. The inset is an expanded view at around the peak of CaHo@C_{82}. (a) Measurement pattern (b) simulated pattern.

Figure 2 shows the mass spectra of two separated CaHo@C_{82} with the simulated mass spectrum patterns of CaHo@C_{82} which is calculated with the natural abundance of Ca, Ho, and C. There is only a large peak at the molecular weight corresponding to CaHo@C_{82}, and the observed peak patterns show very good coincidences with the simulated ones. Therefore, the purifications of two CaHo@C_{82} isomers were confirmed.

As shown in Figures 1d and 1e, both the CaHo@C_{82} isomers elute at ca. 108 min with a 5PBB column. In Figure 1d, the profile after recycling once is shown. It has been known that retention time with a 5PBB column becomes long as the number of π electrons on a cage increases.[8] Capacity factors were calculated on the basis of retention time in Figures 1d and 1e as shown in Figure 3. The line fitted through the cross point by the least-squares method. The capacity factors of two CaHo@C_{82} isomers correspond to 87 π electrons. Therefore, the valence state of C_{82} cage for CaHo@C_{82} is characterized to be pentavalent.

UV–vis–NIR absorption spectra of two CaHo@C_{82} isomers are shown in Figure 4. Absorption spectra of two isomers are different from each other. The pronounced peaks of isomer I and II appear at around 1200 and 900 nm, respectively. The spectral differences can be attributed to their different cage structures. Moreover, these absorption spectra are different from those of any divalent, trivalent, and hexavalent metallofullerenes reported so far.[1,5,6,9,10] This result is consistent with electronic state of $Ca^{2+}Ho^{3+}@C_{82}{}^{5-}$.

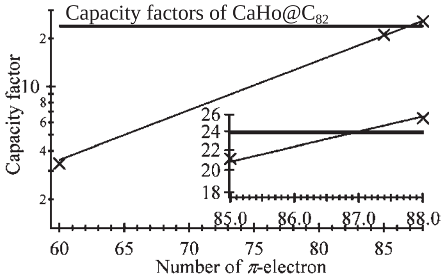

Figure 3. Capacity factor using a 5PBB column with toluene. The inset is an expanded view in the range of 85–88 π-electrons. The horizontal line indicates capacity factor of CaHo@C_{82}. The cross points indicates capacity factor of C_{60}, Ho@C_{82}, and Ca@C_{86}.

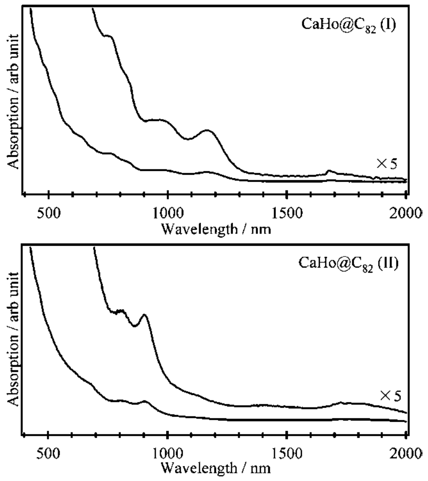

Figure 4. Absorption spectra of two CaHo@C_{82} isomers in CS_2 solution.

In conclusion, we have separated two CaHo@C_{82} isomers by multistep recycling HPLC system. The electronic state of CaHo@C_{82} is deduced to be $Ca^{2+}Ho^{3+}@C_{82}{}^{5-}$, and, therefore, the encapsulation of different metal atoms into a carbon cage is useful for producing metallofullerenes whose cage has unusual valence state.

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References

1 H. Shinohara, *Rep. Prog. Phys.* **2000**, *63*, 843.
2 T. Pichler, M. S. Golden, M. Knupfer, J. Fink, U. Kirbach, P. Kuran, L. Dunsch, *Phys. Rev. Lett.* **1997**, *79*, 3026.
3 R. D. Johnson, M. S. de Vries, J. Salem, D. S. Bethune, C. S. Yannoni, *Nature* **1992**, *355*, 239.
4 R. M. Macfarlane, G. Wittmann, P. H. M. van Loosdrecht, M. de Vries, D. S. Bethune, S. Stevenson, H. C. Dorn, *Phys. Rev. Lett.* **1997**, *79*, 1397.
5 K. Kikuchi, K. Akiyama, K. Sakaguchi, T. Kodama, H. Nishikawa, I. Ikemoto, T. Ishigaki, Y. Achiba, K. Sueki, H. Nakahara, *Chem. Phys. Lett.* **2000**, *319*, 472.
6 K. Akiyama, K. Sueki, T. Kodama, K. Kikuchi, I. Ikemoto, M. Katada, H. Nakahara, *J. Phys. Chem. A* **2000**, *104*, 7224.
7 K. Kikuchi, in *Endofullerenes: A New Family of Carbon Clusters*, ed. by T. Akasaka, S. Nagase, Kluwer Academic Publishers, Dordrecht, The Netherlands, **2002**, p. 217.
8 K. Akiyama, K. Sueki, T. Kodama, K. Kikuchi, Y. Takigawa, H. Nakahara, I. Ikemoto, M. Katada, *Chem. Phys. Lett.* **2000**, *317*, 490.
9 Z. Xu, T. Nakane, H. Shinohara, *J. Am. Chem. Soc.* **1996**, *118*, 11309.
10 K. Yamamoto, H. Funasaka, T. Takahashi, T. Akasaka, T. Suzuki, Y. Masuyama, *J. Phys. Chem.* **1994**, *98*, 12831.

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