# Enrichment of Ce@$C_{60}$ by HPLC Technique

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Endohedral metallofullerene Ce@$C_{60}$ has been enriched in the extracted solution of the soot prepared by arc-heating of CeO/graphite composite rods. The enrichment of Ce@$C_{60}$ in aniline solution containing the hollow and the other endohedral fullerenes have been performed by using high performance liquid chromatography (HPLC) technique. The laser desorption time-of-flight (LD-TOF) mass spectrum shows clearly the enrichment of Ce@$C_{60}$.

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M@$C_{60}$ (M: metal atom) are the most fundamental compounds among the endohedral metallofullerenes, and it is very interesting to study the physical and chemical properties caused by its high symmetry. In 1993 Wang et al. reported the preparation of Ca@$C_{60}$ by laser vaporization of CaO/graphite rods and its extraction with carbon disulfide and pyridine.[1,2] However, no progress in the experimental work has been achieved because of no establishment of the extraction-procedure for Ca@$C_{60}$. In 1995 we reported the preparation of Ca@$C_{60}$ by arc-heating of CaO/ graphite composite rods and its successful extraction with pyridine under oxygen-free condition.[3] Recently we reported the extractions of Ca@$C_{60}$,[4] Sr@$C_{60}$,[4] Ba@$C_{60}$,[5] Y@$C_{60}$,[5] La@$C_{60}$,[5] Ce@$C_{60}$,[5] Pr@$C_{60}$,[5] Nd@$C_{60}$[5] and Gd@$C_{60}$[5] with aniline under an air-atmosphere at low temperature. In the present letter we report the enrichment of Ce@$C_{60}$ by using high performance liquid chromatography (HPLC) technique with aniline as eluent.

The soot containing Ce-endohedral fullerenes was prepared by the arc-heating of $CeO_2$/graphite rods (Toyo Tanso; $CeO_2$ concentration of 0.8 mass %) at 25 V and 80 A under 100 Torr (1 Torr = 133.322 Pa) He atmosphere. The soot was washed with hexane (Wako Pure Chemicals, HPLC available) and then the hollow and endohedral fullerenes were extracted with aniline under ultrasonic irradiation at low temperature from 0 to 5 °C; aniline (Wako Pure Chemicals; GR) was used after distillation under vacuum. The extraction was performed with 0.1 μm membrane filter (Toso; H-13-5) under an air-atmosphere. The extracted solution was separated by using HPLC system (Toso: 8020 detector; CCPS dual pump detector) with aniline eluent and Buckyclutcher I column (Regis Co: 10 mmΦ x 250 mm). A flow rate of eluent was 0.25 ml $min^{-1}$; UV detection was done at 340 nm. Mass spectrum was measured by using a laser desorption time-of-flight (LD-TOF) mass spectrometer (Finnigan Vision 2000) and integrated 50 times; laser desorption and ionization were done at 337 nm. The LD -TOF mass spectrum of soot prepared was the same as that reported previously.[5]

Figure 1(a) shows the LD-TOF mass spectrum of the solution extracted with aniline from the soot containing Ce endohedral fullerenes. Figure 1(b) shows the LD-TOF mass spectrum of the distilled aniline. Many peaks are observed in m/z region from 0 to 500 for both spectra, and these peaks are compatible with each other. Consequently the peaks below 500 originate from the distilled aniline. All peaks above 700 can be assigned to hollow and Ce endohedral fullerenes. The peaks ascribable to Ce@$C_{60}^+$ and Ce@$C_{70}^+$ are very strong, as can be seen from Figure 1(a).

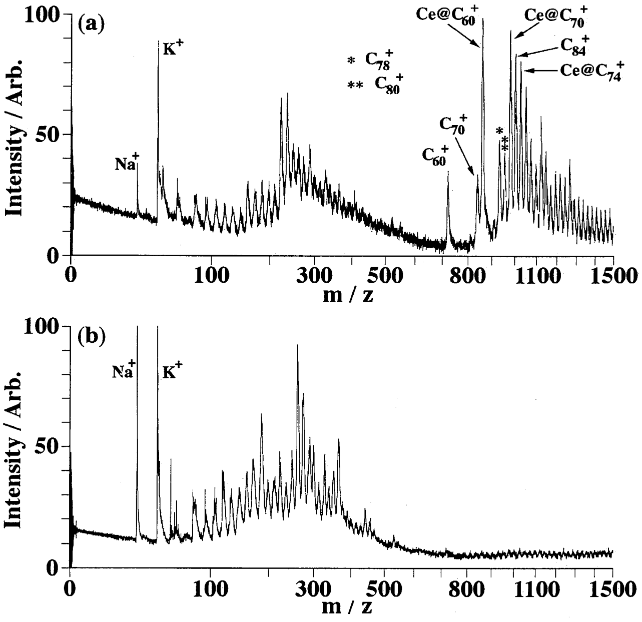

**Figure 1.** LD-TOF mass spectra of (a) aniline extract, and (b) distilled aniline.

Figure 2(a) shows the HPLC profile of aniline extract. The HPLC peak was observed at the retention time from 32.5 to 47.5 min, whose portion was divided into two fractions (I and II). Figure 3(a) shows the LD-TOF mass spectrum of fraction II (37.0 to 39.5 min). A pronounced peak of Ce@$C_{60}^+$ is observed at m/z = 860, as well as weak peaks of hollow fullerenes and Ce endohedral fullerenes such as Ce@$C_{70}^+$ and Ce@$C_{74}^+$. The ratio of the peak intensity for Ce@$C_{70}^+$ to that for Ce@$C_{60}^+$ was 0.36. It shows that the Ce@$C_{60}$ in the solution of fraction II is enriched in comparison with the aniline extract. In the fraction I the peaks of the fullerenes other than Ce@$C_{60}^+$ was stronger than those in fraction II. Furthermore the peak of Ce@$C_{60}$ in the HPLC portion after fraction II decreases with an increase in retention time. Consequently we have concluded that the fraction II in HPLC profile corresponds to Ce@$C_{60}$. The HPLC peaks with maximum at 44.1 and 46.2 min can be attributed to $C_{70}$ and $C_{60}$, respectively.

Figure 2(b) shows the HPLC profile of fraction II. A peak is clearly observed in the region from 37.0 to 42.5 min. We have assigned this peak to Ce@$C_{60}$. The LD-TOF mass spectrum in the fraction II' (37.0 to 39.5 min) is shown in Figure 3(b). A pronounced peak of Ce@$C_{60}^+$ was observed in this spectrum, as

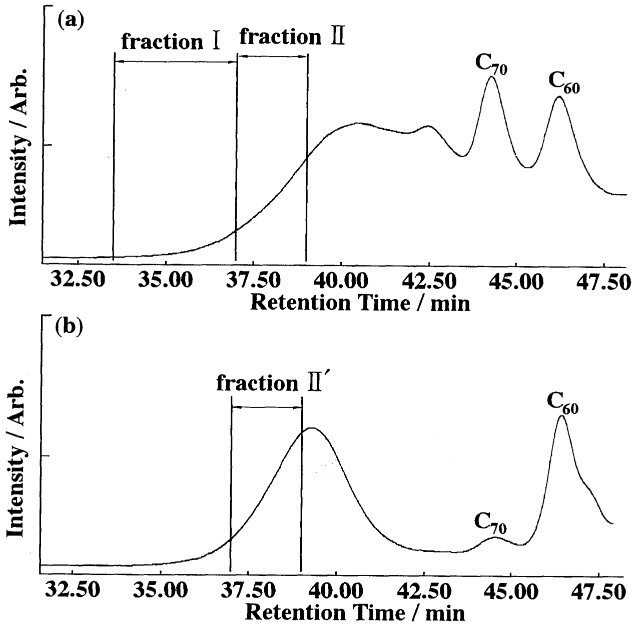

**Figure 2.** HPLC profile of (a) aniline extract, and (b) fraction II.

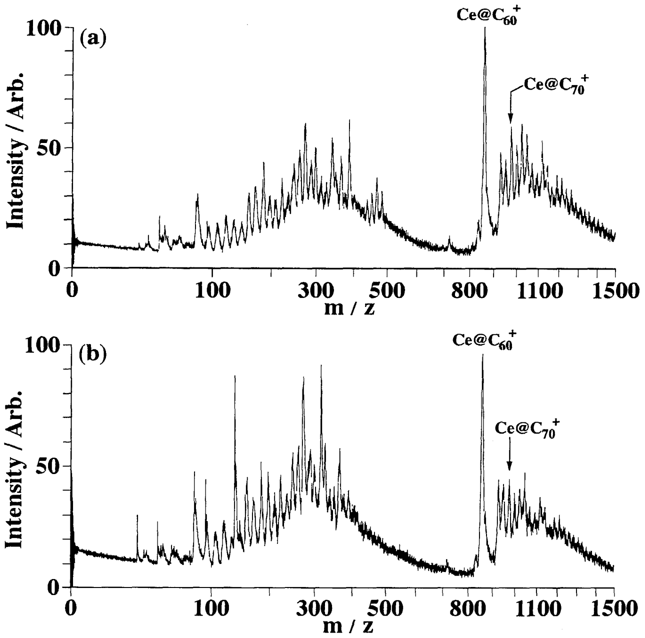

**Figure 3.** LD-TOF mass spectra of (a) fraction II (Figure 2(a)), and (b) fraction II′ (Figure 2(b)).

well as the weak peaks of hollow fullerenes and Ce endohedral fullerenes. The peak-intensities of fullerenes other than $Ce@C_{60}$ decreases slightly in comparison with those in the solution of fraction II; the ratio of the peak intensity for $Ce@C_{70}^+$ to that for $Ce@C_{60}^+$ is 0.27. This fact shows that the $Ce@C_{60}$ is further enriched in the solution of fraction II'. However, the ratio could not further be reduced by repeating the procedure described above. The peak of $C_{60}$ at retention time from 45.0 to 47.5 min was also observed in the HPLC profile of Figure 2(b), though the peak of $C_{60}^+$ in the LD-TOF mass spectrum of fraction II is very weak as can be shown in Figure 3(a). This appears to be contradictive.

From the present work we get two questions why repeating collection of the fraction II does not lead to the perfect isolation, and why the peak of $C_{60}$ is observed in the HPLC profile shown in Figure 2(b). These questions should be resolved by further study. However, the present success in enrichment of $Ce@C_{60}$ gives a clue to its perfect isolation.

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