Synthesis, Extraction and Enrichment of Dy Endohedral Fullerenes

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(Received June 26, 1997; CL-970489)

The Dy endohedral C_{60} ($Dy@C_{60}$) was extracted with aniline under ultrasonic irradiation from the soot prepared by arc-heating of Dy_2O_3/graphite composite rod under He pressure of 80 Torr. The purification of $Dy@C_{60}$ was performed by using high performance liquid chromatography (HPLC) technique. Furthermore, the Dy endohedral C_{82} ($Dy@C_{82}$) was effectively extracted from the soot with N,N-dimethylformamide (DMF).

Metal endohedral C_{60} ($M@C_{60}$, M: atom) are very interesting compounds. However the experimental studies on $M@C_{60}$ are scarcely reported because of the difficulty of its extraction and isolation. In 1993 Wang et al. first reported the extraction of $Ca@C_{60}$ from the soot prepared by laser vaporization of CaO/graphite rod with carbon disulfide and pyridine.[1,2] We also reported the preparation of $Ca@C_{60}$ by arc-heating of CaO/graphite composite rod and its successful extraction with pyridine under oxygen-free condition.[3] Recently we succeeded in the extraction 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 and their enrichment by high performance liquid chromatography (HPLC) technique with aniline as eluent.[6,7] Furthermore we tried to prepare, extract and purify other lanthanide endohedral C_{60}. In this study we have for the first time succeeded in the synthesis, extraction and enrichment of $Dy@C_{60}$. The studies have scarcely been carried out even for Dy endohedral C_{82} ($Dy@C_{82}$) as well as $Dy@C_{60}$, since $Dy@C_{82}$ has not effectively been extracted by toluene.[8] In the present letter, we report the synthesis, extraction and enrichment of $Dy@C_{60}$, and also report the effective extraction of $Dy@C_{82}$ with N,N-dimethylformamide (DMF).

The raw soot was prepared by arc-heating of Dy_2O_3/graphite rod (Toyo Tanso; Dy_2O_3 concentration of 0.8 mass %) at 25 V and 80 A under 80 Torr (1 Torr = 133.322 Pa) He atmosphere, which was the best condition for preparation of the raw soot.[4-7] The obtained soot was washed with hexane (Wako Pure Chemicals, HPLC use) and then the hollow and endohedral fullerenes were extracted with DMF (Wako Pure Chemicals; HPLC use) or with aniline (Wako Pure Chemicals; GR); the extraction was achieved with DMF by Soxhlet-extraction for 25 h or with aniline by ultrasonic irradiation for 3 h at temperatures from 0 to 5 °C. The extracted solution was passed through 0.5 μm membrane filter (Toso; H-25-5) under air-atmosphere.

The DMF and toluene (Wako Pure Chemicals, HPLC use) were used without further purification, and aniline was used after distillation under vacuum. The $Dy@C_{60}$ was enriched 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 0.3 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.

In the LD-TOF mass spectrum for the raw soot, the pronounced peaks for $Dy@C_{60}^+$ and $Dy@C_{70}^+$ were observed with the weak peaks for DyC_{60+2n}^+; the peaks for C_{60}^+ and C_{70}^+ were very weak. A clear peak for $Dy@C_{82}^+$ in the LD-TOF mass spectrum for the DMF-extracted solution from the soot was observed with those for C_{60}^+, C_{70}^+ and $Dy@C_{80}^+$; the peak assigned to $Dy@C_{80}^+$ may be due to the photofragment of $Dy@C_{82}$ upon laser desorption / ionization. The peaks for $Dy@C_{60}^+$ and $Dy@C_{70}^+$ were not observed in this spectrum. Gillan et al. have already reported that $Dy@C_{82}$, $Dy_2@C_{80}$ and $Dy_2@C_{84}$ can be extracted with toluene but the observed mass spectrum is very weak.[8] The present results show that DMF is very effective for the extraction of $Dy@C_{82}$ in the same manner as $Ce@C_{82}$ and $Nd@C_{82}$.[9,10] Figure 1(a) shows the LD-TOF mass spectrum for the toluene solution of DMF-extract. A clear peak for $Dy@C_{82}^+$ was observed with that for $Dy@C_{80}^+$.

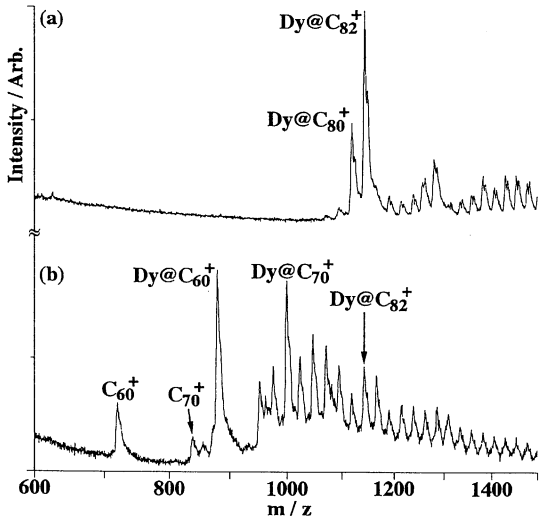

Figure 1. LD-TOF mass spectra for (a) the toluene solution of DMF-extract and (b) the aniline-extracted solution.

Figure 1(b) shows the LD-TOF mass spectrum for the aniline-extracted solution from the soot. The pronounced peaks for $Dy@C_{60}^+$ and $Dy@C_{70}^+$ were observed with the peaks for DyC_{60+2n}^+. The aniline can effectively extract $Dy@C_{60}$ and $Dy@C_{70}$. The second intense peak ($Dy@C_{70}^+$) was 0.95 times as intense as the peak for $Dy@C_{60}^+$. The peaks for C_{60}^+ and C_{70}^+ were very weak in this spectrum.

Figure 2(a) shows the HPLC profile of aniline-extract. The HPLC peak was observed in the retention time from 30.0 to 55.0 min. The portion in the retention time from 31.0 to 36.0 min was collected. The intense peak in the retention time from 36.0 to 44.0 min could be assigned to Dy endohedral higher fullerenes, and then the peaks in the retention time from 44.0 to 49.0 min and from 49.0 to 52.0 min were assigned to C_{60} and C_{70}, respectively. Figure 2(b) shows the LD-TOF mass spectrum for the collected fraction. A pronounced peak for $Dy@C_{60}^+$ was observed at m/z = 883, as well as weak peaks of DyC_{66+2n}^+. In this spectrum the peak for $Dy@C_{70}^+$ decreases drastically in

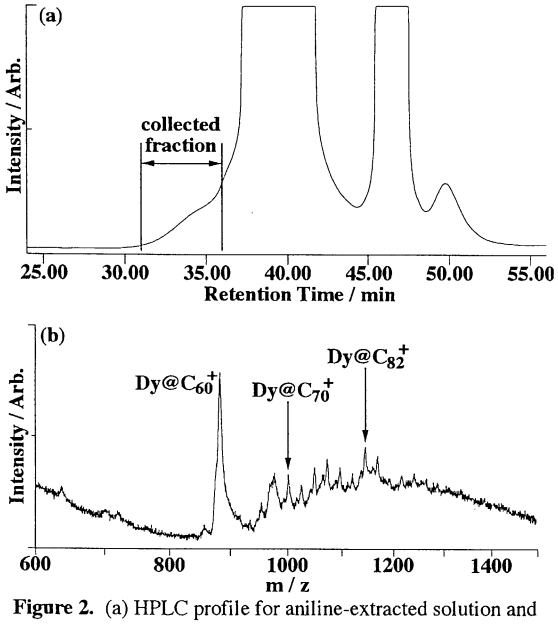

Figure 2. (a) HPLC profile for aniline-extracted solution and (b) LD-TOF mass spectrum for the collected fraction shown in (a).

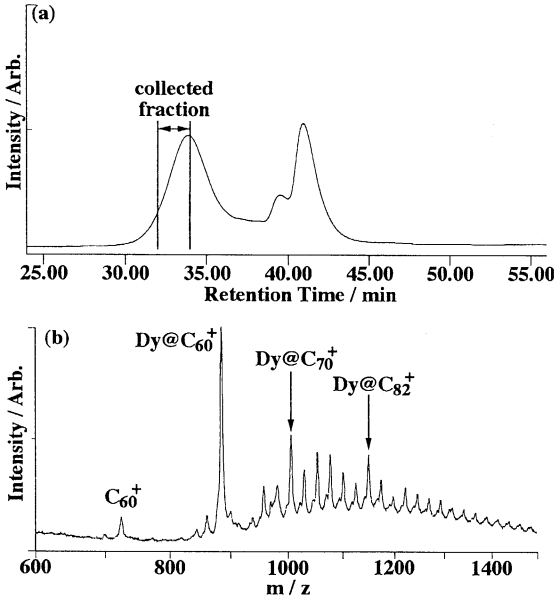

Figure 3. (a) HPLC profile for the collected fraction shown in Figure 2(a), and (b) LD-TOF mass spectrum for the collected fraction shown in (a).

comparison with that for aniline-extract. The second intense peak can be assigned to $Dy@C_{82}^+$. The ratio of the peak intensity for $Dy@C_{82}^+$ to that for $Dy@C_{60}^+$ was 0.55. It shows that $Dy@C_{60}$ in the collected fraction is enriched in comparison with the aniline-extract.

Figure 3(a) shows the HPLC profile for the collected fraction shown in Figure 2(a). A clear peak in the region from 31.0 to 36.0 min was observed with two peaks in the region 38.0 - 42.5 min. The peak in the region from 30.0 to 36.0 min was assigned to $Dy@C_{60}^+$ from the LD-TOF mass spectrum shown in Figure 3(b). A pronounced peak for $Dy@C_{60}^+$ was observed in this spectrum, as well as the weak peaks of DyC_{66+2n}^+. Though the peak due to C_{60}^+ was not observed in Figure 2(b), the peak was observed in Figure 3(b). The increase in peak-intensity due to C_{60}^+ may be ascribed to the decomposition of $Dy@C_{60}^+$. The ratio of the peak intensity for the second intense peak ($Dy@C_{70}^+$) to that for $Dy@C_{60}^+$ was 0.49. This fact shows that the purification of $Dy@C_{60}$ is slightly improved by repeating HPLC procedure twice. Consequently, it is necessary to use another procedure for achieving the complete separation of $Dy@C_{60}$.

It has been found that the $Dy@C_{60}$ enriched solution can be obtained by HPLC with Buckyclutcher I column and aniline as eluent. Although the complete separation of $Dy@C_{60}$ could not be achieved, the success in enrichment of $Dy@C_{60}$ and effective extraction of $Dy@C_{82}$ can give a clue to the isolation of $Dy@C_{60}$ and $Dy@C_{82}$. By the way, in this paper, the DyC_{60}, DyC_{70} and DyC_{82} whose cages satisfy IPR rule are regarded as endohedral fullerenes, $Dy@C_{60}$, $Dy@C_{70}$ and $Dy@C_{82}$, though a critical evidence for " endohedral" should be obtained by X-ray structure analyses.

References and Notes

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