Communications to the Editor

Extractions of Y@C_{60}, Ba@C_{60}, La@C_{60}, Ce@C_{60}, Pr@C_{60}, Nd@C_{60}, and Gd@C_{60} with Aniline

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Recently many endohedral metallofullerenes such as M@C_{74}, M@C_{80}, and M@C_{82} (M: metal atom) have been successfully isolated by the high performance liquid chromatography (HPLC) technique.[1−5] Some M@C_{60} were prepared in primary soots by an arc-heating or a laser-vaporization method,[6−9] but the isolation of M@C_{60} has not yet been achieved because of the difficulties in extraction; only the extraction of Ca@C_{60} with pyridine has been reported so far.[10,11] Recently we found that aniline is a suitable extraction solvent for Ca@C_{60} and Sr@C_{60}.[12] For the isolation of M@C_{60} by an HPLC technique it is important to find a suitable extraction solvent for M@C_{60}. In the present study, we report the successful extraction of Y@C_{60}, Ba@C_{60}, La@C_{60}, Ce@C_{60}, Pr@C_{60}, Nd@C_{60}, and Gd@C_{60} with aniline under an air atmosphere.

The soots containing M@C_{60} (M: Y, Ba, La, Ce, Pr, Nd and Gd) were prepared by the arc-heating of the M_xO_y/graphite (M_xO_y: $x = 2$ and $y = 3$ except for BaO, CeO_2, and Pr_6O_{11}) rods (Toyo Tanso; M concentration: 0.8 mol % except for Ba (0.3 mol %)) at 25 V and 80 A under 100 T of He atmosphere. We then tried 48 solvents[13] to extract Ca@C_{60}, but had success only with aniline and pyridine. Therefore the extraction of M@C_{60} was tried with aniline (Wako Pure Chemicals: GR) as well as three representative solvents of benzene, toluene (Wako Pure Chemicals: GR), and CS_2 (Ishidzu Seiyaku: GR) under air atmosphere. The soot was dissolved in these solvents by ultrasonic irradiation at low temperatures from 0 to 5 °C for 3 h, and the resulting solutions were passed through a 0.1 μm membrane filter (Toso: H-13-5). Mass spectra were measured by a laser desorption time-of-flight (LD-TOF) mass spectrometer (Finnigan: Vision 2000): laser desorption and ionization were done at 337 nm.

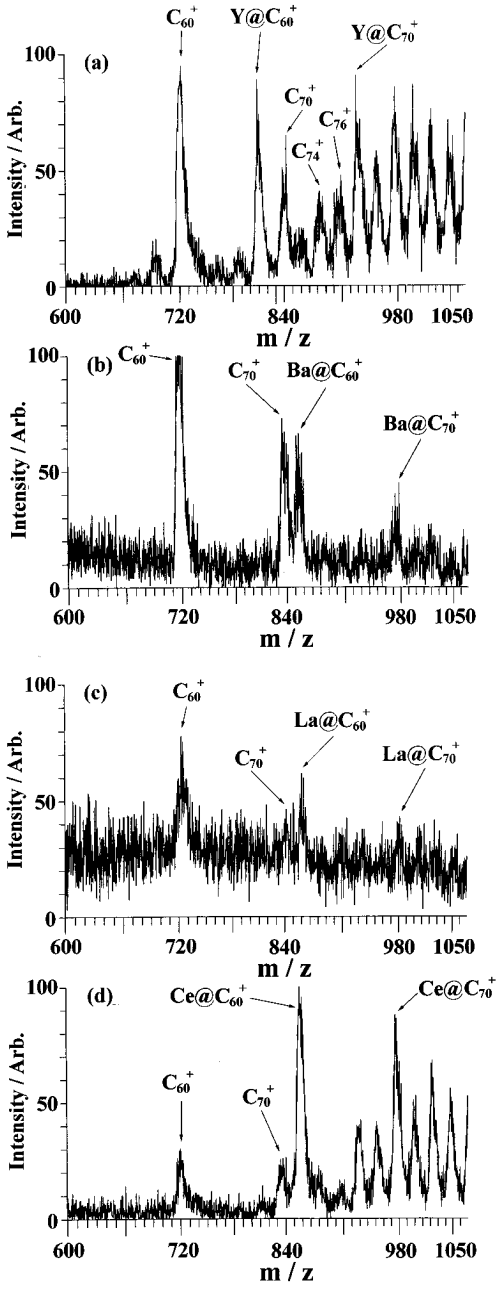

Figure 1. LD-TOF mass spectra for the aniline solutions extracted from the soots containing (a) Y@$_{60}$, (b) La@C_{60}, (c) Ba@C_{60}, and (c) Ce@C_{60}.

Parts a−d in Figure 1 show the LD-TOF mass spectra of the aniline-extracted solutions from the soots containing Y@C_{60}, Ba@C_{60}, La@C_{60} and Ce@C_{60}, respectively. After extraction, the peaks for Y@C_{60}^+ and Y@C_{70}^+ have nearly the same intensity as the corresponding hollow fullerenes, as shown in Figure 1a. However, the ratio of the peak intensities for C_{60}^+

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(13) Names of 48 solvents are deposited.

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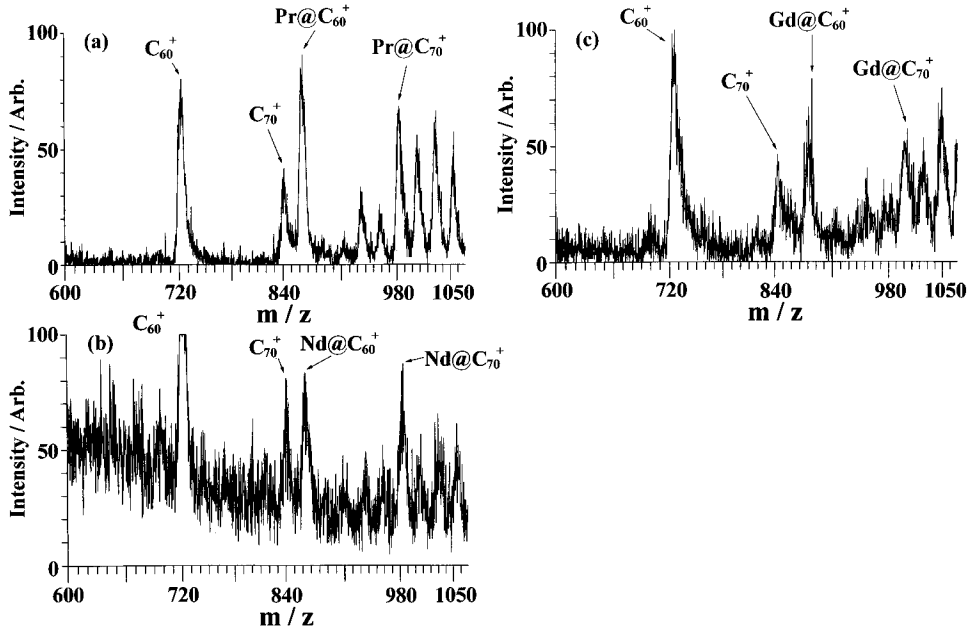

Figure 2. LD-TOF mass spectra for the aniline solutions extracted from the soots containing (a) $Pr@C_{60}$, (b) $Nd@C_{60}$, and (c) $Gd@C_{60}$.

and C_{70}^+ to those for $Y@C_{60}^+$ and $Y@C_{70}^+$ is larger in the aniline extract than in the soot.[14] The results show the relatively higher extractability of these hollow fullerenes in aniline. The peaks for C_{60}^+, C_{70}^+, $Ba@C_{60}^+$, and $Ba@C_{70}^+$ are observed in the spectrum in Figure 1b. The intensity of the peak for $Ba@C_{60}^+$ is almost the same as that for C_{70}^+; the peak for C_{60}^+ is the most intense. This shows that the extractability of $Ba@C_{60}$ in aniline is lower than that of C_{60}, but nearly equal to that of C_{70}. The peaks for the other hollow fullerenes are not observed in this spectrum. Two peaks for C_{60}^+ and $La@C_{60}^+$ are clearly observed in Figure 1c; the other peaks are very weak. In Figure 1d, the peaks for $Ce@C_{60}^+$ and $Ce@C_{70}^+$ are much more intense than those for the other fullerenes.

Parts a−c in Figure 2 show the LD-TOF mass spectra of the aniline solutions extracted from the soots containing $Pr@C_{60}$, $Nd@C_{60}$, and $Gd@C_{60}$, respectively. The intense peaks for C_{60}^+, $Pr@C_{60}^+$, and $Pr@C_{70}^+$ are observed in the spectrum in Figure 2a. The relative peak intensities of C_{60}^+, $Pr@C_{60}^+$, and $Pr@C_{70}^+$ are almost the same as those in the primary soot.[14] The results indicate that the extractability of $Pr@C_{60}$ and $Pr@C_{70}$ in aniline is as high as that of C_{60}. The peaks for C_{60}^+, C_{70}^+, $Nd@C_{60}^+$, and $Nd@C_{70}^+$ are observed in the spectrum in Figure 2b. The ratio of the intensity of the peak for C_{60}^+ to that for $Nd@C_{60}^+$ increases greatly after the extraction. In Figure 2c, the peaks for C_{60}^+, C_{70}^+, $Gd@C_{60}^+$, and $Gd@C_{70}^+$ are observed. The relative intensity of the peak for C_{60}^+ increases as observed in Figure 2b.

We found that aniline is an effective extraction solvent for $M@C_{60}$. The LD-TOF mass spectra of the solutions extracted from the soots with benzene, toluene, and CS_2 showed the peaks for hollow fullerenes, but no peaks for metallofullerenes. This discovery of a suitable extraction solvent aniline for $M@C_{60}$ in the present study is a breakthrough in the isolation of $M@C_{60}$.

Supporting Information Available: Names of 48 solvents and the LD-TOF mass spectra for the primary soots (3 pages). See any current masthead page for ordering and Internet access instructions.

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(14) The LD-TOF mass spectra for the primary soots are deposited.