

A Simple Method for the Selective Enrichment of Endohedral Metallofullerenes

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The concentration of a polar solvent DMF extract was found to be very effective for the selective enrichment of endohedral metallofullerenes against empty fullerenes. As the solvent evaporated, endohedral metallofullerenes were effectively enriched in the solution, while most of empty fullerenes (especially C₆₀ and C₇₀) were precipitated because of their scant solubility in DMF. Matrix-assisted laser-desorption–ionization time-of-flight mass spectrometry analysis indicated that the purity of endohedral metallofullerenes increased dramatically after concentration of the DMF extract solution. Upon transferring the extract into toluene, a solution containing significantly enriched endohedral metallofullerenes was obtained. The different solubilities of endohedral metallofullerenes versus empty fullerenes are considered to account for this selective enrichment of endohedral metallofullerenes.

Introduction

One of the spectacular directions of fullerene research involves encapsulation of metal atom(s) inside the fullerene cage to form metal@fullerene endohedral complexes, or metallofullerenes. Since the first observation of metallofullerenes La@C_{2n} by Smalley's group in 1985,¹ these exotic molecules have attracted intense interest owing to their unique "super-atom" structures and great application prospects.^{2–4} The utilization of the arc evaporation technique makes it possible to synthesize metallofullerenes in macroscopic quantities,^{5,6} which can be further purified by HPLC separation.^{7–10} As a

result, some studies on their molecular and electronic structures, chemical derivatization, and application have been carried out.^{11–24}

However, the isolation of metallofullerenes in large quantities remains rather difficult and inefficient. The minuscule content of endohedral metallofullerene species overwhelmed by the much more abundant empty fullerenes in the solvent extract of the carbon soot makes the subsequent HPLC isolation step especially demanding. This situation has greatly hindered further characterization of these interesting species. It is thus very important to find some methods which can enrich

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metallofullerenes effectively. In this paper, we report an effective method to enrich endohedral metallofullerenes for HPLC isolation. With a simple concentration of a DMF extract, the purity of metallofullerenes increases drastically, because most of the empty fullerenes were removed by precipitation. By using this method, we obtained a toluene solution which contains significantly enriched endohedral metallofullerenes, making the HPLC isolation very efficient and convenient.

Experimental Section

Soot containing metallofullerenes was produced by the standard arc vaporization method. As an example, gadolinium metallofullerenes, $Gd_n@C_{2,m}$, were chosen in the present work. A i.d. 6×100 mm graphite rod was drilled to generate a deep cylindrical hole concentric with the rod (i.e., i.d. 4×70 mm) and filled with a mixture of Gd_2O_3 (purity of 99.99%) and graphite powder with an atomic ratio of $Gd/C = 1:100$. The rod was baked at $1200^\circ C$ in a vacuum for 8 h to turn the metal oxide into metal carbide. The composite rod thus prepared was vaporized as an anode in an arc discharge soot generator. The following are the dc arc discharge conditions: voltage, 25–30 V; current, 75–90 A; He pressure, 100 Torr. After the composite rod was consumed, the arc polarity was reversed to “back burn” the metal carbide-rich cathode deposit.²⁵ Finally, the soot was collected.

In a typical run, 10 g of raw soot was Soxhlet extracted with *N,N*-dimethylformamide (DMF) at its boiling point for 20 h under N_2 atmosphere. Water and oxygen were excluded during the extraction. The DMF extract appeared dark brown. After evaporation of DMF, ~1% of the raw soot by weight was obtained. For the concentration experiment, part of the extract was concentrated by vacuum evaporation at $50^\circ C$ to 10% of its original volume and kept under N_2 atmosphere. After 1 h, some precipitates appeared, the concentrated DMF extract was filtered, and the solution part was retained. A simple estimation showed that ~80% of the DMF extract precipitated upon concentration. The concentrated solution contained ~15 mg of soot, from which about 5 mg of metallofullerenes could be isolated. A matrix-assisted laser-desorption/ionization time-of-flight mass spectrometer (MALDI-TOF MS, Biochemistry Instrument Co., Ltd.) was used for the analysis of the DMF extract before and after the concentration treatment. The extract was dropped onto a Cu target, and the solvent was evaporated in a vacuum, leaving a layer of sample on the target surface. Samples were desorbed and ionized by a nitrogen laser (337 nm) without the assistance of any matrix. The laser beam was attenuated to a low energy (ca. 4–7 μJ) to avoid fragmentation. The negative ions were collected for at least 30 single shots.

For HPLC isolation, the concentrated DMF extract was transferred into a toluene solution. All the DMF solvent was evaporated under reduced pressure at $50^\circ C$, and a black powder was obtained. This black powder was then redissolved in toluene, and the soluble fraction was injected into an HPLC. A buckyprep column ($4.6 \text{ mm} \times 250 \text{ mm}$; Cosmosil, Nacalai Tesque Inc.) was used for the HPLC isolation. The mobile phase was toluene. The injection volume was 1 mL and the elution rate was 1.0 mL/min.

Results and Discussions

Figure 1 shows the negative-ion LD-TOF mass spectrum of the primary DMF extract. The peaks due to the empty fullerenes C_{60} (m/z 720), C_{70} (m/z 840), and C_{84} (m/z 1008) are dominant, and the peak from the endohedral metallofullerene $Gd@C_{82}$ (m/z 1141) is also

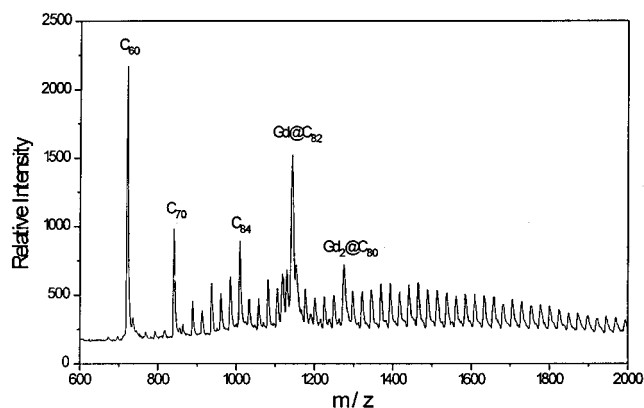


Figure 1. Negative-ion LD-TOF mass spectrum of the primary DMF extract solution.

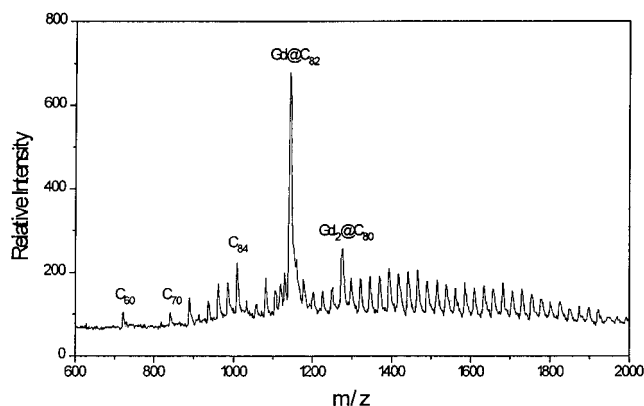


Figure 2. Negative-ion LD-TOF mass spectrum of the concentrated DMF extract solution.

appreciable. This demonstrates the efficiency of the DMF extraction as reported previously.²⁶ However, the purity of the endohedral metallofullerenes is not very high. Figure 2 shows the negative-ion LD-TOF mass spectrum of the concentrated DMF extract. As described in the Experimental Section, the concentrate was obtained by vacuum evaporation at $50^\circ C$. It is clear that most of the empty fullerenes have been removed. As a result, the purity of the endohedral metallofullerenes has increased dramatically. In particular, the endohedral metallofullerene $Gd@C_{82}$ was effectively and selectively enriched in the concentrated DMF extract.

This method for effective enrichment of endohedral metallofullerenes made the HPLC isolation step much more convenient and efficient. By using this method, only one-step HPLC is needed to isolate submilligram metallofullerenes in a very short time. A 5 mg sample of pure metallofullerenes could be obtained in a few days from soot production to the final HPLC separation. The overall yield of metallofullerenes is ~0.05%. This was limited by the amount of metallofullerenes available in the soot. Figure 3 shows the HPLC chromatogram of the toluene solution from the concentrated DMF extract. The assignment of the main peaks indicated in the figure was confirmed by negative ion desorption chemical ionization mass spectrometry. Remarkably, the peaks of empty fullerenes C_{60} and C_{70} are very small, while the peak of the endohedral metallofullerene $Gd@C_{82}$ is dominant. The apparent purity of endohedral

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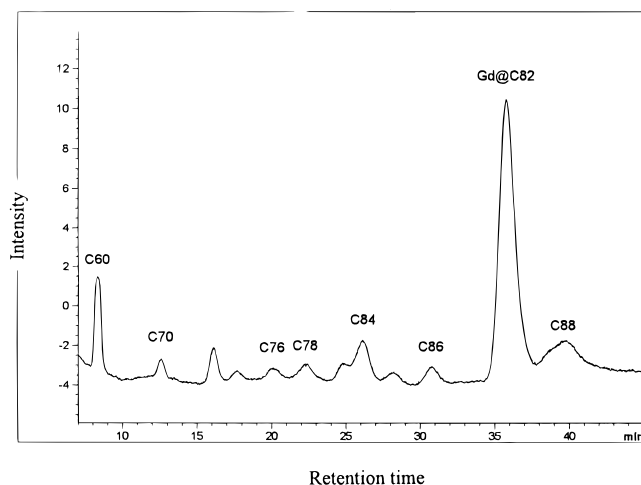


Figure 3. HPLC chromatogram of the toluene solution of the concentrated DMF extract.

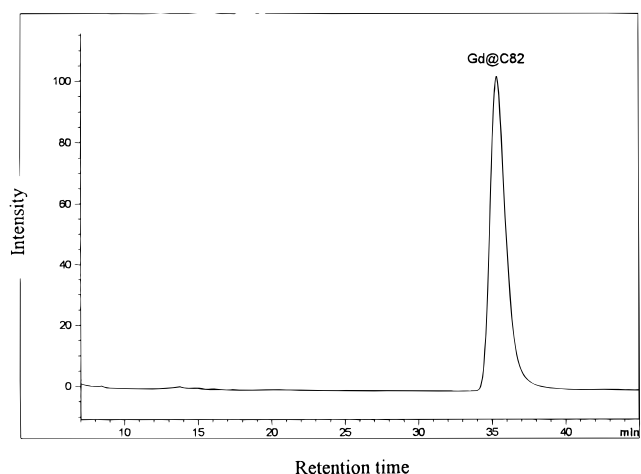


Figure 4. HPLC chromatogram of the endohedral metallofullerene $Gd@C_{82}$ collected from the toluene solution of the concentrated DMF extract.

metallofullerenes in the concentrated extract was estimated to be more than over 50% according to the HPLC analysis. However, this estimate does not consider any differences in the extinction coefficient between the metallofullerene and the empty fullerenes. Figure 4 shows an HPLC chromatogram of the isolated endohedral metallofullerene $Gd@C_{82}$ collected from Figure 3. The purity of endohedral metallofullerene $Gd@C_{82}$ was estimated to be $\sim 99.5\%$.

How can a simple concentration of the DMF extract selectively and effectively enrich the endohedral metallofullerenes? We believe that the effective metallofullerene enrichment is due to the different solubilities of the endohedral metallofullerenes from those of the empty fullerenes. Upon concentration, the empty fullerenes with low solubilities recrystallize. As is well-known, the encapsulated metal atom(s) occupy an off-center position in the fullerene cage, and approximately three electrons are transferred from each trapped metal atom to the fullerene cage.²⁷ This makes the metal-carbon bonds highly polarized, leading to the strong solvation of the metallofullerenes by polar solvents. It is interest-

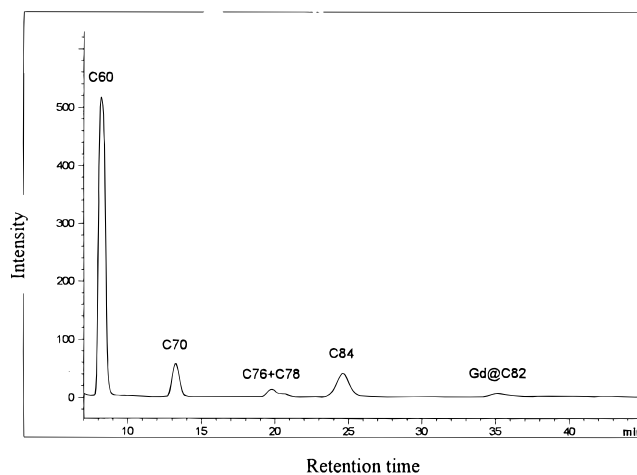


Figure 5. HPLC chromatogram of the toluene solution of the precipitates obtained from the concentration of the DMF extract solution.

ing to note that $Gd_2@C_{80}$ has no dipole moment due to the opposite polarity of the metal-carbon bonds of the two metal atoms. Due to the relatively large size of the metallofullerene, however, the localized regions of the polarized metal-carbon bonds can also be strongly solvated by polar solvents. Therefore, metallofullerenes prefer to dissolve in such polar solvents as DMF and pyridine.²⁸

On the other hand, the solubilities of empty fullerenes in these polar solvents is limited, especially for the highly symmetric C_{60} and C_{70} molecules. When the DMF extract is concentrated by solvent evaporation, the empty fullerenes become supersaturated, and most of them are recrystallized and become precipitates. Therefore, simple concentration can remove C_{60} and C_{70} as well as giant fullerenes, notably C_{84} . However, the removal efficiencies of C_{60} and C_{70} are much higher than those of the giant fullerenes because C_{60} and C_{70} are highly symmetric and they have lower polarizabilities than the giant fullerenes have. Consequently, their solubilities in polar solvents are much lower. Figure 5 shows the HPLC chromatogram of the toluene solution of the precipitates obtained from the concentrated DMF extract. It contains mainly empty fullerenes C_{60} , C_{70} , and C_{84} but little endohedral metallofullerene $Gd@C_{82}$. This suggests that the amount of the dissolved endohedral metallofullerenes has not suffered significant reduction during the concentration. In other words, most of the endohedral metallofullerenes are still left in the concentrated solution because they have larger solubilities in DMF during the concentration. Thus, the purity of the metallofullerenes increases dramatically.

For the same reason, an experiment with another polar solvent, dimethyl sulfoxide (DMSO), gave a similar result. The negative-ion LD-TOF mass spectra of the primary and concentrated DMSO extracts are quite similar. It is obvious that the purity of the endohedral metallofullerenes increased significantly after the concentration of the DMSO extract. On the contrary, concentration of the toluene (nonpolar solvent) extract reduced the content of endohedral metallofullerene

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significantly, while no measurable reduction of the empty fullerenes occurred.

In summary, we have demonstrated a simple concentration procedure to effectively enrich endohedral metallofullerenes in a DMF extract. This method makes use of the different solubilities of metallofullerenes and empty fullerenes in DMF. Upon the concentration of the extract, the empty fullerenes were removed by precipitation, leaving the bulk of metallofullerenes in the solution. By using this simple method, one can ef-

fectively enrich endohedral metallofullerenes in a polar solvent solution.

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