Isolation and Characterization of Er@C_{60}

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Endohedral metallofullerenes[1,2] are a novel form of fullerene-related materials having unique geometrical and electronic structures. Production, isolation, and characterization of a variety of metallofullerenes have been performed during recent years since the first macroscopic production of La@C_{82}[3] and the first isolation of metallofullerenes, Sc_2@C_{84}[4] and La@C_{82}.[5] Although the production and solvent extraction of C_{60}-based metallofullerenes, M@C_{60} (M = metal atom), have been reported,[6−9] the isolation of M@C_{60}-type metallofullerenes has not been realized. Endohedral metallofullerenes so far isolated are limited to higher fullerene-based metallofullerenes such as C_{82} and C_{84}.[1,2] This is largely because M@C_{60} is unstable in air and soluble only in such solvents as pyridine[6,7] and aniline[9] which are not suited for HPLC mobile phases. Here, we report the first purification and isolation of a C_{60}-based endohedral metallofullerene, Er@C_{60}, via a combined technique of vacuum sublimation followed by high-performance liquid chromatographic (HPLC) separation. It has been observed that Er@C_{60} is significantly more stable than La@C_{60} at vacuum sublimation at temperatures of 400−450 °C.

Soot containing Er@C_{60}, Er@C_{70}, and other erbium higher metallofullerenes (Er@C_{72} to Er@C_{120}) was produced in direct-current (500 A, 28 V) arc discharge of the high temperature (1200 °C)-treated erbium/graphite composite rods (Toyo Tanso Co. Ltd., 15 × 15 × 300 mm, 0.8 atomic %) under He flow (8−10 L/min) at 50 Torr. The soot was collected under totally anaerobic conditions in an upper chamber filled with dry nitrogen directly connected to a lower arc discharge chamber.[2,4,10] The obtained soot was sublimed in a vacuum (8×10^{-6} Torr) at 400−450 °C for 30−40 min to obtain Er@C_{60}-rich fullerenes of typically 5−10 mg. The sublimed fullerene sample was dissolved in a degassed aniline by ultrasonication. The aniline solution was then subjected to HPLC separation on a Buckyclutcher-I column (10 mm diameter × 250 mm, Regis Tech. Inc.)[2,4] with a 100% aniline eluent. Prior to HPLC injection, the aniline solution was filtered by a 0.2 μm membrane filter to remove insoluble residues. The final purified Er@C_{60} material was ca. 1.5 mg.

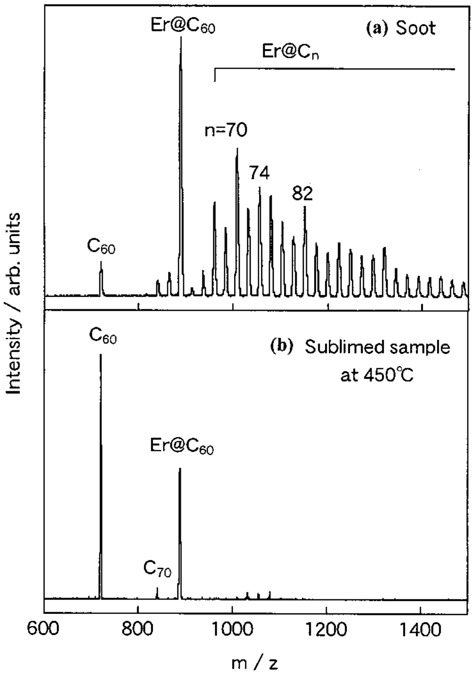

Figure 1. Laser-desorption TOF mass spectra at 355 nm of (a) as-produced soot and (b) a sublimed sample at 450 °C. The intensities of Er@C_{2n} metallofullerenes are enhanced with respect to those of empty fullerenes in this positive mass spectra because of their higher multiphoton desorption/ionization efficiency.

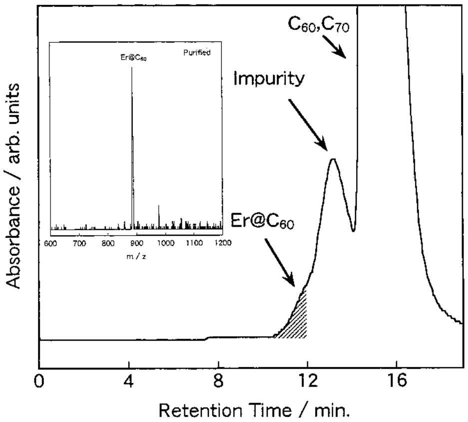

Figure 2. An HPLC chromatogram of aniline extract of the sublimed soot (cf. Figure 1b) with a Buckyclutcher-I column (1.0 mL/min; 330 nm detection; 100% aniline eluent). The insert gives a LD-TOF mass spectrum of the onset fraction (shaded area) showing a single peak due to Er@C_{60}.

Figure 1, panels a and b, shows laser-desorption (LD) time-of-flight (TOF) positive mass spectra at 355 nm of as-produced and sublimed soot at 450 °C, respectively. The as-produced soot shows a series of Er@C_{2n} ($60 \le 2n \le 110$) metallofullerenes with an enhanced peak at Er@C_{60}, whereas the sublimed soot contains only C_{60} and Er@C_{60} together with a small amount of C_{70}. This indicates that the major portion of the fullerenes in primary soot which can sublime at 450 °C is only C_{60} and Er@C_{60} and that the other empty and endohedral fullerenes have much higher sublimation temperatures.

The onset of the sublimation temperature of Er@C_{60} (ca. 370 °C) is a bit higher than that of C_{60} (350 °C) but lower than those of the higher empty and endohedral fullerenes. This enables us to separate only Er@C_{60} and C_{60} from other fullerenes in soot.

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(1) Bethune, D. S.; Johnson, R. D.; Salem, J. R.; de Vries, M. S.; Yannoni, C. S. *Nature* **1993**, *366*, 123.

(2) Shinohara, H. *Advances in Metal and Semiconductor Clusters*; Duncan, M., Ed.: JAI Press: Greenwich, CT, 1998; Vol. 4, pp 205−226.

(3) Chai, Y.; Guo, T.; Changming, Jin.; Haufler, R. E.; Chibante, L. P. F.; Fure, J.; Wang, L.; Alford, J. M.; Smalley, R. E. *J. Phys. Chem.* **1991**, *95*, 7564.

(4) Shinohara, H.; Yamaguchi, H.; Hayashi, N.; Sato, H.; Ohkohchi, M.; Ando, Y.; Saito, Y. *J. Phys. Chem.* **1993**, *97*, 4259.

(5) Kikuchi, K.; Suzuki, S.; Nakao, Y.; Nakahara, N.; Wakabayashi, T.; Shiromaru, H.; Saito, I.; Ikemoto, I.; Achiba, Y. *Chem. Phys. Lett.* **1993**, *216*, 67.

(6) Wang, L. S.; Alford, J. M.; Chai, Y.; Diener, M.; Zhang, J.; McClure, S. M.; Guo, T.; Scuseria, G. E.; Smalley, R. E. *Chem. Phys. Lett.* **1993**, *207*, 354.

(7) Wang, L. S.; Alford, J. M.; Chai, Y.; Diener, M.; Smalley, R. E. *Z. Phys. D* **1993**, *26*, S297.

(8) Kubozono, Y.; Ohta, T.; Hayashibara, T.; Maeda, H.; Ishida, H.; Kashino, S.; Oshima, K.; Yamazaki, H.; Ukita, S.; Sogabe, T. *Chem. Lett.* **1995**, 457.

(9) Kubozono, Y.; Maeda, H.; Takabayashi, Y.; Hiraoka, K.; Nakai, T.; Kashino, S.; Emura, S.; Ukita, S.; Sogabe, T. *J. Am. Chem. Soc.* **1996**, *118*, 6998.

(10) Shinohara, H.; Takata, M.; Sakata, M.; Hashizume, T.; Sakurai, T. *Mater. Sci. Forum* **1996**, *232*, 207.

10.1021/ja992665a CCC: $19.00

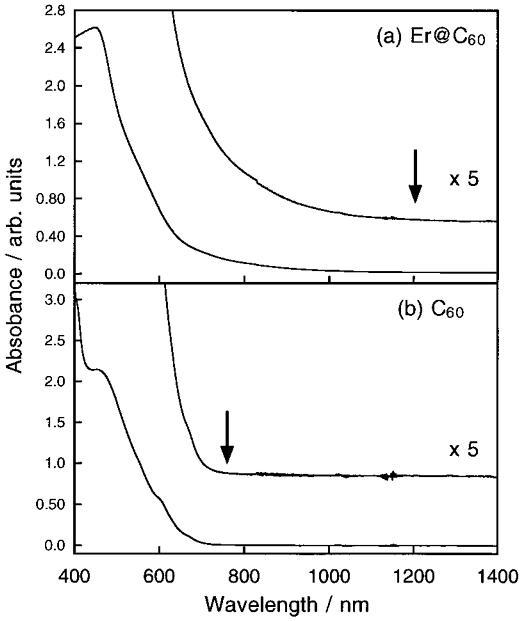

Figure 3. UV−vis−near-IR absorption spectra of (a) isolated Er@C_{60} in aniline solution and (b) C_{60} in aniline solution. The absorption onsets are indicated by arrows.

In fact, a mass spectrum of the sublimed soot at a higher temperature of 500 °C exhibits strong peaks due to C_{70}, Er@C_{72}, Er@C_{74}, Er@C_{76}, and Er@C_{82} comparable to Er@C_{60} (not shown). A similar temperature dependence on sublimation behavior was reported for La@C_{60} and higher lanthanum metallofullerenes.[11]

Figure 2 exhibits a Buckyclutcher HPLC chromatogram of aniline extract of the sublimed sample. The HPLC profile is quite different from the conventional HPLC profile with toluene eluent: the overall profile is broad and shows a limited HPLC resolution, indicating small fullerene−column interactions with the aniline mobile phase. However, LD-TOF mass analyses indicated that the intense peak is predominantly due to C_{60} and a small amount of C_{70} and that a small peak at 13 min corresponds to impurities present in aniline solvent. We have identified that the small shoulder at the onset of the chromatogram (the shaded area between 10.5 and 12 min in retention time) is entirely due to Er@C_{60}. The final isolation of Er@C_{60} was thus achieved by collecting this HPLC fraction. The resultant mass spectrum is presented as an insert in Figure 2 showing a single peak due to Er@C_{60}.

A UV−vis−near-IR absorption spectrum of Er@C_{60} in aniline is shown in Figure 3. The spectrum has a characteristic peak at 500 nm and has the onset at 1200 nm, which is far in the red compared to that of C_{60} in aniline. Since the metallofullerenes are better electron acceptors[12,13] than the empty fullerenes, Er@C_{60} presumably forms weak charge-transfer complexes with aniline molecules in solution.[14,15] Er@C_{60} could be stabilized by forming these complexes in aniline solution.

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Supporting Information Available: Details of laser-desorption/ionization mass spectral analyses on the separated HPLC (high-performance liquid chromatography) fractions of Er@C_{60} and various higher Er-metallofullerenes (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Diener, M. D.; Smith, C. A.; Veirs, D. K. *Chem. Mater.* **1997**, *9*, 1773.

(12) Suzuki, T.; Maruyama, Y.; Kato, T.; Kikuchi, K.; Achiba, Y. *J. Am. Chem. Soc.* **1993**, *115*, 11006.

(13) Diener, M. D.; Alford, J. M. *Nature* **1998**, *393*, 668.

(14) Li, J.; Feng, J.; Sun, C. *J. Phys. Chem.* **1994**, *98*, 8636.

(15) Skiebe, A.; Hirsch, A.; Klos, H.; Gotschy, B. *Chem. Phys. Lett.* **1994**, *220*, 138.