

Efficient *N,N*-Dimethylformamide Extraction of Endohedral Metallofullerenes for HPLC Purification

Junqi Ding and Shihe Yang*

Department of Chemistry, Hong Kong University of Science and Technology,
Clear Water Bay, Kowloon, Hong Kong

Received June 3, 1996. Revised Manuscript Received August 7, 1996[®]

A new and efficient extraction method using DMF (*N,N*-dimethylformamide) was developed to concentrate endohedral metallofullerenes. This single-step extraction method obtained a solution containing 5–15% endohedral metallofullerenes and strongly discriminated against the dominant C₆₀, C₇₀, and higher empty fullerenes in raw soot. This highly selective extraction procedure substantially reduced sample loading in the HPLC isolation for a given volume of sample injection. The efficiency of our separation method is demonstrated by the isolation of the endohedral metallofullerene Ce@C₈₂.

Introduction

During the past three years there has been a surge of research activity in the isolation and characterization of endohedral metallofullerenes.^{1–3} With the increasing availability of endohedral metallofullerene samples accompanying the advance of metallofullerene separation techniques more and more properties of the various endohedral metallofullerenes have been characterized.^{1–3} The most recent developments include the revelation of the monoclinic structure of Y@C₈₂ by X-ray diffraction,⁴ exohedral derivatization of La@C₈₂,⁵ electrochemistry of the less common metallofullerene La₂@C₈₀,⁶ and the FT-EPR of La@C₈₂.⁷

However, the preparation of milligram amounts of endohedral metallofullerenes (~95% purity) is still very time consuming and solvent consuming and involves multistep chromatographic procedures.^{8–13} This results from a most annoying limiting factor in HPLC separa-

tion of endohedral metallofullerenes that in various fullerene solvent extracts empty fullerenes (mainly C₆₀ and C₇₀) are usually above 2 orders of magnitude more abundant than the endohedral metallofullerenes. One way to circumvent this problem is to improve the HPLC column for higher loading capacity while maintaining a reasonable selectivity.¹⁴ Another solution, which is perhaps more convenient and cost-effective, is to raise the extraction selectivity toward the metallofullerenes. High-pressure toluene extraction succeeded to some extent in this regard but did not attract widespread use.¹⁵ Kappes et al. reported an enhancement of extraction efficiency of metallofullerenes by mixing the dipolar solvent CH₃OH into CS₂.¹³ In our efforts to separate endohedral metallofullerenes we have also noted a prominent difference in dipole moment between empty fullerenes and endohedral metallofullerenes. By exploiting the dipole moment difference, we have successfully developed an efficient extraction scheme to separate endohedral metallofullerenes.

In this work we report this new and efficient extraction scheme which uses DMF to concentrate endohedral metallofullerenes. A simple one-step extraction obtained a solution containing 5–10% endohedral metallofullerenes and strongly discriminated against the dominant C₆₀, C₇₀, and higher empty fullerenes in the raw soot. This highly selective extraction procedure reduced the sample loading in the HPLC isolation by at least an order of magnitude in comparison with other extraction solvents used to date. The efficiency of our separation method is demonstrated by the isolation of a new endohedral metallofullerene, Ce@C₈₂. Instead of LDMS, we used DCI negative ion mass spectrometry to estimate the purity of our metallofullerene samples. DCI negative ion mass spectrometry is known to reflect

* To whom correspondence should be addressed.

[®] Abstract published in *Advance ACS Abstracts*, September 15, 1996.

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

(2) Edelmann, F. T. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 981.

(3) Fuchs, D.; Rietschel, H.; Michel, R. H.; Benz, M.; Fischer, A.; Kappes, M. M. In: *Proc. IWEPM 95*; Fink, J.; Kuzmani, H.; Mehring, M.; Roth, S., Eds.; World Scientific: Singapore, 1995.

(4) Takata, M.; Umeda, B.; Nishibori, E.; Sakata, M.; Saito, Y.; Ohno, M.; Shinohara, H. *Nature* **1995**, *377*, 46.

(5) Akasaka, T.; Kato, T.; Kobayashi, K.; Nagase, S.; Yamamoto, K.; Funasaka, H.; Takahashi, T. *Nature* **1995**, *374*, 600.

(6) Suzuki, T.; Maruyama, Y.; Kato, T.; Kikuchi, K.; Nakao, Y.; Achiba, Y.; Kobayashi, K.; Nagase, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1094.

(7) (a) Okabe, N.; Ohba, Y.; Suzuki, S.; Kawata, S.; Kikuchi, K.; Achiba, Y.; Iwaizumi, M. *Chem. Phys. Lett.* **1995**, *235*, 564. (b) Rubsam, M.; Pluschau, M.; Schweitzer, P.; Dinse, K.-P.; Fuchs, D.; Rietschel, H.; Michel, R. H.; Benz, M.; Kappes, M. M. *Chem. Phys. Lett.* **1995**, *240*, 615.

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

(9) Yamamoto, K.; Funasaka, H.; Takahashi, T.; Akasaka, T. *J. Phys. Chem.* **1994**, *98*, 2008.

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

(11) (a) Stevenson, S.; Dorn, H. C.; Burbank, P.; Harich, K.; Haynes, Jr., J.; Kiang, C. H.; Salem, J. R.; DeVries, S.; van Loosdrecht, P. H. M.; Johnson, R. D.; Yannoni, C. S.; Bethune, D. S. *Anal. Chem.* **1994**, *66*, 2675. (b) Stevenson, S.; Dorn, H. C.; Burbank, P.; Harich, K.; Sun, Z.; Kiang, C. H.; Salem, J. R.; DeVries, S.; van Loosdrecht, P. H. M.; Johnson, R. D.; Yannoni, C. S.; Bethune, D. S. *Anal. Chem.* **1994**, *66*, 2680.

(12) Shinohara, H.; Kishida, M.; Nakane, T.; Kato, T.; Bandow, S.; Saito, Y.; Wang, X.; Hashizume, T.; Sakurai, T. In: *Fullerenes: Recent Advances in the Chemistry and Physics of Fullerenes*; Kadish, K., Ruoff, R. S., Eds.; ECS: San Francisco, 1994; p 1361.

(13) Fuchs, D.; Rietschel, H.; Michel, R. H.; Fischer, A.; Weis, P.; Kappes, M. M. *J. Phys. Chem.* **1996**, *100*, 725.

(14) Xiao, J.; Savina, M. R.; Martin, G. B.; Francis, A. H.; Meyerhoff, M. E. *J. Am. Chem. Soc.* **1994**, *116*, 9341.

(15) Capp, C.; Wood, T. D.; Marshall, A. G.; Coe, J. V. *J. Am. Chem. Soc.* **1994**, *116*, 4987.

the relative abundance of compositions of fullerenes and metallofullerenes with a reasonable accuracy.¹⁶

Experimental Section

Soot containing metallofullerenes was produced by the standard arc vaporization method using a composite anode which contained graphite and cerium in its oxide or carbide form. Graphite powder (99.999%, Alfa) and CeO₂ (99.95%, Shanghai Chemicals Inc.) in an atomic ratio of Ce/C = 0.01 were uniformly mixed with a graphite cement (GC grade, Dylon Inc.). The mixture was pressed into a 6 mm diameter (10 cm long) rod under a hydraulic pressure of 3000 kg/cm². After curing at 140 °C for 4 h, the rod was heated to 1100 °C in a vacuum for 4 h. The rod was then subjected to a dc discharge under an He atmosphere of 50 Torr. The raw soot was collected and extracted in a Soxhlet extractor using *N,N*-dimethylformamide (DMF, 99.9%, BDH) under N₂ atmosphere. A yellowy green color was observed immediately after the extraction started, indicating the transfer of fullerenes from the soot to the solution. Over a period of 1 h, 90% of the metallofullerenes could be extracted. But normally we extracted the soot for 8 h. After removal of DMF by evaporation, a black powder (~1% of the raw soot) was obtained. The soluble fraction was dissolved in toluene and injected into an HPLC. A buckyprep column (4.6 mm × 250 mm; Cosmosil, Nacalai Tesque Inc.) similar to a PYE column was used, and the mobile phase was toluene. The injection volume was 1 mL and the elution rate was 1.0 mL/min. DCI negative ion mass spectrometry (Finnigan TSQ7000) was used to characterize the composition of the samples.

When the extraction process was carried out in the ambient condition, the extraction yield was reduced. Upon air exposure of the redissolved sample in toluene from the DMF extraction, the HPLC peak of Ce@C₈₂ also decreased. However, the exposure of the raw soot to air before extraction did not reduce the isolation yield of Ce@C₈₂ significantly.

Results and Discussion

Shown in Figure 1a is an HPLC profile for the crude extract of the fullerene soot redissolved in toluene. A prominent peak appears at the elution time of 34 min, which is absent for samples produced from arc-discharge of a pure-carbon electrode. This peak clearly corresponds to Ce@C₈₂ as verified by mass spectrometry shown in Figure 2 which will be described below. Note that the Ce@C₈₂ peak in Figure 1a is quite strong in comparison with the strongest peak C₆₀. The integrated peak area of Ce@C₈₂ is estimated to be ~15% of all the species present in the HPLC profile. This is the highest ratio obtained by a single HPLC run after a single-step extraction. Normally, soot extracted using other solvents contains only 0.1–0.5% endohedral metallofullerenes. Note that the relative magnitude of higher empty fullerene peaks adjacent to Ce@C₈₂ in Figure 1a is substantially lower than that in most previous studies using other solvents for extraction. This made possible a single-step HPLC isolation of endohedral metallofullerenes with ~99.5% purity.

Figure 1b shows an HPLC profile of the collected fraction of Ce@C₈₂ in Figure 1a. The spectrum shows a single clean peak due to Ce@C₈₂, indicating the efficiency of our single-step isolation. With the type of column we are using, M@C₈₂ (M = rare-earth elements) is usually merged together with C₈₈, making the separation difficult.⁹ However, the C₈₈ present was reduced to a negligible amount in this case since even the

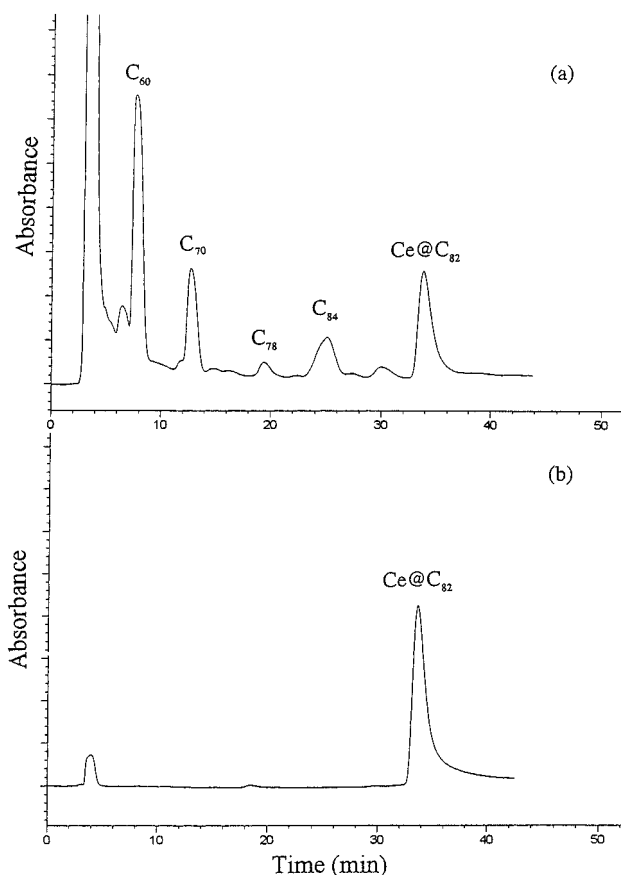


Figure 1. (a) HPLC chromatogram of the redissolved crude DMF extract from the metallofullerene soot. Note the comparable intensities of C₆₀, C₇₀, and Ce@C₈₂. (b) HPLC chromatogram of Ce@C₈₂ collected from (a). Note that only one clean peak appears corresponding to Ce@C₈₂. The peaks at 3.5 min in (a) and (b) are due to the solvent. 330 nm UV detection was used.

amount of the much more abundant C₇₈ and C₈₄ fullerenes is less than that of Ce@C₈₂.⁹

Figure 2a shows the mass spectrum of a redissolved DMF extract of the metallofullerene soot. It can be seen that the intensities of the mass spectrum approximately reflect the intensities of the corresponding HPLC chromatogram (Figure 1a). Figure 2b shows the mass spectrum of the fraction of Ce@C₈₂ collected after a single-step HPLC. It is remarkable that the spectrum contains only a single peak corresponding to Ce@C₈₂. Isotopic ratio analysis is consistent with this assignment. This confirms that the peak in Figure 1b is indeed pure Ce@C₈₂. The intensity of C₆₀ is nearly 3 orders of magnitude smaller than that of Ce@C₈₂, suggesting that the purity of Ce@C₈₂ is ~99.5%. Experiments on other rare-earth elements obtained similar results. Details on the separation and characterization of these metallofullerenes will be reported elsewhere.¹⁷

Presumably, the selectivity of DMF to preferentially extract metallofullerenes derives from the large dipole moment of DMF (3.82 D). This is consistent with theoretical calculations that predict that La@C₈₂ pos-

(16) Dunsch, L.; Kirbach, U.; Klostermann, K. *J. Mol. Struct.* **1995**, 348, 381.

(17) (a) Ding, J. Q.; Weng, L. T.; Yang, S. H. *J. Phys. Chem.* **1996**, 100, 11120. (b) Ding, J. Q.; Yang, S. H. *Angew. Chem., Int. Ed. Engl.*, in press. (c) Ding, J. Q.; Lin, N.; Weng, L. T.; Cue, N.; Yang, S. H. *Chem. Phys. Lett.*, in press. (d) Ding, J. Q.; Yang, S. H. *J. Am. Chem. Soc.*, in press.

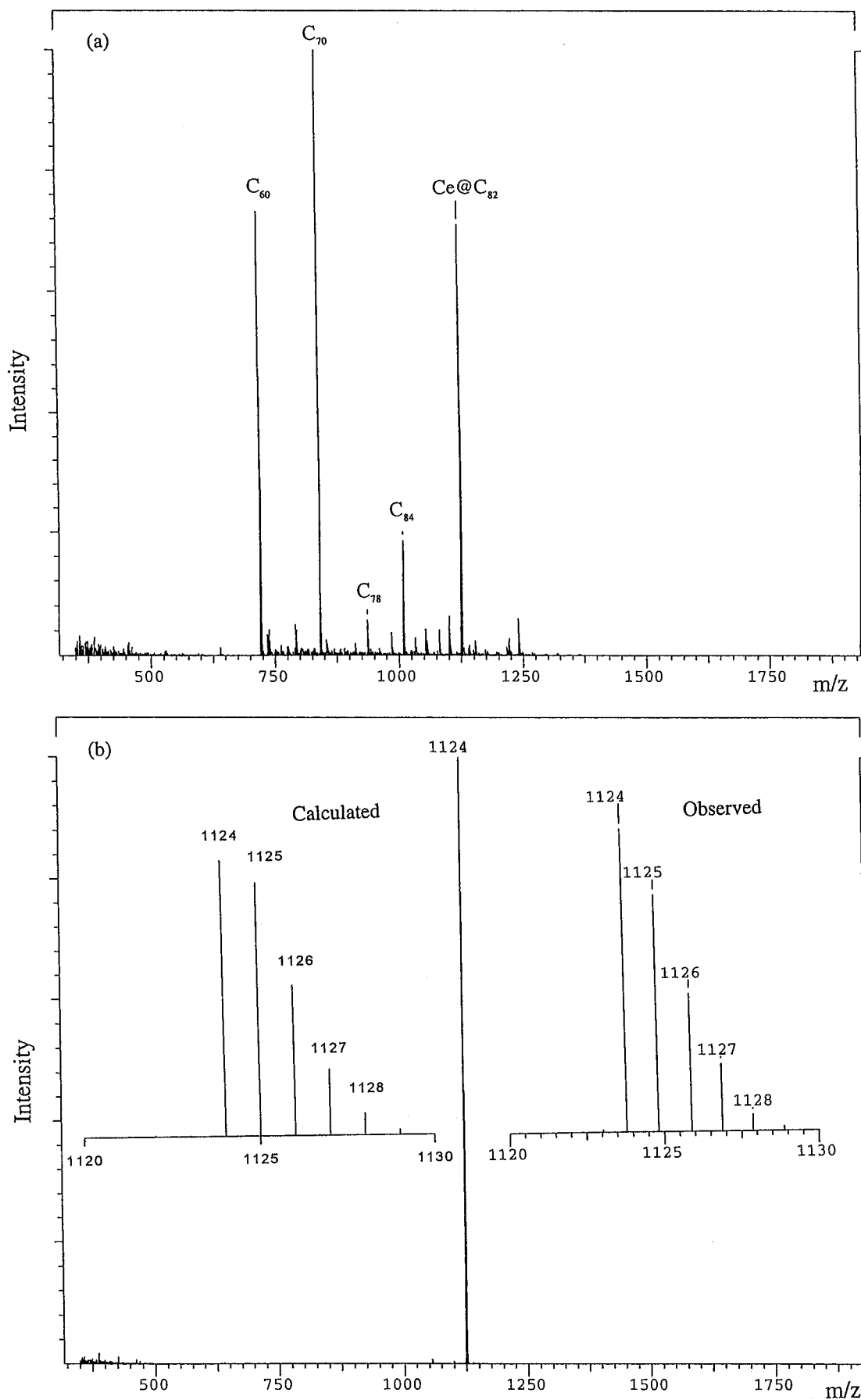


Figure 2. (a) Methane DCI negative ion mass spectrum of the sample corresponding to Figure 1a before HPLC separation. (b) Methane DCI negative ion mass spectrum of the sample corresponding to Figure 1b after HPLC separation. The insets show the calculated and observed isotopic distribution for $Ce@C_{82}$.

sesses a dipole moment of 3–4 D.¹⁸ Recent experiments also showed that adding dipolar CH₃OH into CS₂ for extraction increased the relative concentration of metallofullerenes.¹³

Of all the solvents (e.g., toluene, CS₂, 1,2,4-trichlorobenzene, pyridine, etc.) we have tested for the extraction of the metallofullerenes M@C₈₂ (M = rare-earth metal), DMF appears to be one of the best in terms of its extraction selectivity for M@C₈₂. As for pyridine as an extraction solvent for Ce@C₈₂, we obtained similar results as reported by Xiao et al.¹⁴ However, pyridine is also a relatively good solvent for higher fullerenes, and this may cause the difficulty in the final HPLC separation of M@C₈₂. In addition, due to its unpleasant smell, pyridine is not in particular a solvent of choice.

(18) (a) Laasonen, K.; Andreoni, W.; Parrinello, M. *Science* **1992**, *258*, 1916. (b) Poirier, D. M.; Knupfer, M.; Weaver, J. H.; Andreoni, W.; Laasonen, K.; Parrinello, M.; Bethune, D. S.; Kikuchi, K.; Achiba, Y. *Phys. Rev. B* **1994**, *49*, 17403.

Conclusion

The presently reported experiment demonstrated that selective extraction of metallofullerenes is possible by taking advantage of the dipole moment difference between empty fullerenes and metallofullerenes. This significantly reduces the time and cost of the separation procedures for obtaining a given amount of metallofullerenes. By using this separation method, we have successfully isolated several other new metallofullerenes Ce₂@C₈₀, Nd@C₈₂, Pr@C₈₂, etc. Some of their properties have been characterized.¹⁷

Acknowledgment. This work is supported by an RGC Grant (HKUST601/95P) administrated by the UGC of Hong Kong. The technical assistance of Miss Rowena Leung is appreciated. We are grateful to Dr. Ben Tang for allowing us to use his instruments. We thank Dr. D. S. Bethune and Dr. M. M. Kappes for sending their manuscripts on metallofullerenes.

CM960318J