

Reduction of Endohedral Metallofullerenes: A Convenient Method for Isolation

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Isolation of the endohedral metallofullerenes is currently carried out via a multistage high-performance liquid chromatography (HPLC) method. However, this method is tedious and time-consuming work, making it difficult to obtain macroscopic quantities of pure endohedral metallofullerenes. We report herein a selective electrochemical reduction of the endohedral metallofullerenes from extracts of carbon soot and a convenient separation method of endohedral metallofullerenes and empty fullerenes. A chemical oxidation of the endohedral metallofullerene anions is also discussed.

Introduction

Endohedral metallofullerenes are of interest as new molecules and materials with novel electronic properties and reactivities which are not observed for empty fullerenes.¹ Endohedral metallofullerenes are more easily reduced than empty fullerenes.¹ The difference in redox potential is in fact the most important difference between endohedral metallofullerenes and empty fullerenes. The electronic properties and reactivity of endohedral metallofullerenes² are therefore different from those of empty fullerenes.

Among endohedral metallofullerenes, La-metallofullerenes have been recognized as a prototype of endohedral metallofullerenes since their first successful extraction in 1991 by Smalley and co-workers.³ The isolation of endohedral metallofullerenes is currently

carried out via multistage high-performance liquid chromatography (HPLC) method.^{4,5} However, this method is a tedious and time-consuming process, making it difficult to obtain macroscopic quantities of purified endohedral metallofullerenes. Meanwhile, although enrichment of endohedral metallofullerenes by the methods of electrochemical reduction,⁶ sublimation followed by chemical oxidation,⁷ chemical reduction,⁸ or dimethylformamide extraction of soot⁹ has been reported and the selective redox-based procedure has been used to purify endohedral metallofullerenes from the soot,¹⁰ the isolation of pure endohedral metallofullerenes has not yet been accomplished by these methods.

Recently, we reported the electrochemical reduction of La@C₈₂-A,¹¹ La@C₈₂-B,¹² and Pr@C₈₂-A¹³ to verify structures of the electrogenerated diamagnetic anions by ¹³C NMR measurements. These anions show both a

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(1) For recent reviews, see: (a) Kobayashi, K.; Nagase, S. In *Endofullerenes: A New Family of Carbon Clusters*; Akasaka, T., Nagase, S., Eds.; Kluwer Academic Publishers: Dordrecht, 2002; pp 99–119. (b) Wakahara, T.; Akasaka, T.; Kobayashi, K.; Nagase, S. In *Endofullerenes: A New Family of Carbon Clusters*; Akasaka, T., Nagase, S., Eds.; Kluwer Academic Publishers: Dordrecht, 2002; pp 231–251. (c) Nagase, S.; Kobayashi, K.; Akasaka, T.; Wakahara, T. In *Fullerenes: Chemistry, Physics and Technology*; Kadish, K., Ruoff, R. S., Eds.; John Wiley & Sons: New York, 2000; pp 395–436. (d) Shinohara, H. *Rep. Prog. Phys.* **2000**, *63*, 843. (e) Nagase, S.; Kobayashi, K.; Akasaka, T. *J. Comput. Chem.* **1998**, *19*, 232. (f) Nagase, S.; Kobayashi, K.; Akasaka, T. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2131. (g) Bethune, D. S.; Johnson, R. D.; Salem, J. R.; de Vries, M. S.; Yannoni, C. S. *Nature* **1993**, *366*, 123.

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

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

(4) (a) Yamamoto, K.; Funasaka, H.; Takahashi, T.; Akasaka, T. *J. Phys. Chem.* **1994**, *98*, 2009. (b) Yamamoto, K.; Funasaka, H.; Takahashi, T.; Akasaka, T.; Suzuki, T.; Maruyama, Y. *J. Phys. Chem.* **1994**, *98*, 12831.

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

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

(7) Bolskar, R. D.; Alford, J. M. *Chem. Commun.* **2003**, 1292.

(8) Sun, B.; Gu, Z. *Chem. Lett.* **2002**, 1164.

(9) (a) Sun, B.; Feng, L.; Shi, Z.; Gu, Z. *Carbon* **2002**, *40*, 1591. (b) Bubnov, V. P.; Laukhina, E. E.; Kareev, I. E.; Koltov, V. K.; Prokhorova, T. G.; Yagubskii, E. B.; Kozmin, Y. P. *Chem. Mater.* **2002**, *14*, 1004.

(10) Diener, M. D.; Bolskar, R. D.; Alford, J. M. In *Endofullerenes: A New Family of Carbon Clusters*; Akasaka, T., Nagase, S., Eds.; Kluwer Academic Publishers: Dordrecht, 2002; pp 133–151.

(11) Akasaka, T.; Wakahara, T.; Nagase, S.; Kobayashi, K.; Waelchli, M.; Yamamoto, K.; Kondo, M.; Shirakura, S.; Okubo, S.; Maeda, Y.; Kato, T.; Kako, M.; Nakadaira, Y.; Nagahata, R.; Gao, X.; Van Caemelbecke, E.; Kadish, K. M. *J. Am. Chem. Soc.* **2000**, *122*, 9316.

(12) Akasaka, T.; Wakahara, T.; Nagase, S.; Kobayashi, K.; Waelchli, M.; Yamamoto, K.; Kondo, M.; Shirakura, S.; Maeda, Y.; Kato, T.; Kako, M.; Nakadaira, Y.; Gao, X.; Van Caemelbecke, E.; Kadish, K. M. *J. Phys. Chem. B* **2001**, *105*, 2971.

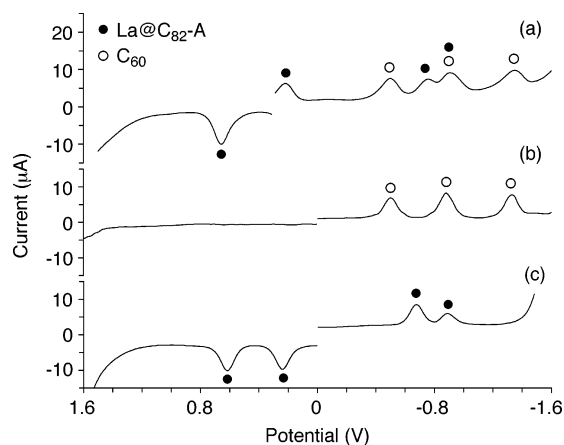
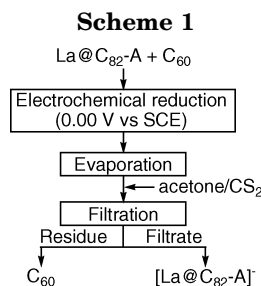


Figure 1. Differential pulse voltammograms of (a) a mixture of La@C₈₂-A and C₆₀, (b) C₆₀, and (c) [La@C₈₂-A][−] isolated in Scheme 1. Samples were measured in ODCB at a scan rate of 20 mV s^{−1} with 0.03 M *n*-Bu₄NClO₄ as supporting electrolyte at a Pt working electrode vs SCE.



high stability and a high solubility; that is, they are soluble in polar solvents such as mixed acetone/CS₂ and are insoluble in nonpolar solvents such as toluene and CS₂. This contrasts with what is seen for neutral fullerenes which are insoluble in polar solvents and soluble in nonpolar solvents. In this paper, we report a convenient method for the isolation of endohedral metallofullerenes from solvent-extracts of carbon soot, in which selective reduction of the endohedral metallofullerenes with low redox potentials takes place. Reduced endohedral metallofullerene and neutral empty fullerenes may thus be separated via utilization of their different solubilities.

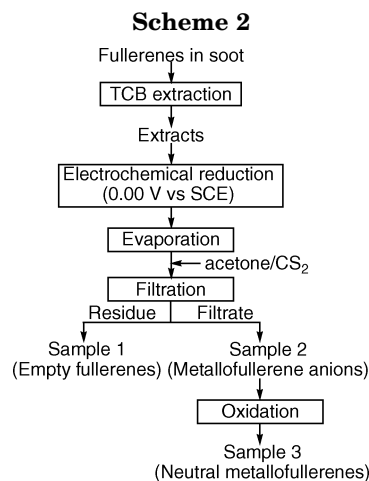
Results and Discussion

Separation of C₆₀ and La@C₈₂. Initially, we investigated the separation of a mixture of C₆₀ and La@C₈₂-A as shown in Scheme 1. Figure 1a shows a differential pulse voltammogram of the 1:1 mixture (3.0×10^{-4} M) in *o*-dichlorobenzene (ODCB) containing 3.0×10^{-2} M *n*-Bu₄NClO₄ as supporting electrolyte. A controlled-potential bulk reduction of the mixture was carried out utilizing a previously described method.^{11–13} The potential was held constant at 0.00 V relative to a saturated calomel electrode (SCE). Because C₆₀ and La@C₈₂-A have first reduction potentials of −0.55 and 0.15 V, respectively (see Table 1), La@C₈₂-A is the only species reduced selectively by bulk electrolysis at this applied potential. The visible and near-infrared (vis-

Table 1. Redox Potentials^a and Reactivity toward Electrochemical Reduction of Endohedral Metallofullerenes and Empty Fullerenes

compd	reduction ^b	ox E_1 /V	red E_1 /V
La@C ₈₂ -A	yes	0.64	0.15
La@C ₈₂ -B	yes	0.50	0.10
La ₂ @C ₈₀	yes	1.13	0.26
C ₆₀	no	1.78	−0.55
C ₇₀	no	1.76	−0.52
C ₇₆	no	1.30	−0.43
C ₇₈	no	1.52	−0.20
C ₈₂	no	1.29	−0.12
C ₈₄	no	1.45	−0.17

^a Potentials vs SCE. Conditions: 0.1 M *n*-Bu₄NPF₆ in *o*-dichlorobenzene; working electrode, Pt disk (1 mm diameter); counter electrode, Pt wire. CV: scan rate, 20 mV s^{−1}. ^b Reactivity toward electrochemical reduction at 0.00 V vs SCE.



NIR) spectrum of the resulting solution shows an absorption maximum at 934 nm characteristic of the La@C₈₂-A anion ([La@C₈₂-A][−]).¹¹ After removal of ODCB, the resulting precipitate was washed with a mixture of acetone/CS₂ (=4:1), and the residue was dissolved in CS₂. Differential pulse voltammetry (Figure 1b and c), vis-NIR, and laser desorption-time-of-flight (LD-TOF) mass measurements of the resulting solutions reveal that [La@C₈₂-A][−] and C₆₀ are separated completely into the acetone/CS₂ and CS₂ solutions in 87% and 95% yields, respectively. On the basis of this successful separation, we applied the method to the isolation of endohedral metallofullerenes and empty fullerenes from the extract of raw soot as shown in Scheme 2.

Isolation of La-Metallofullerenes from Solvent-Extracts of Carbon Soot. The La-metallofullerenes in soot produced by an improved arc-discharge method⁴ were extracted with 1,2,4-trichlorobenzene (TCB). The LD-TOF mass and ESR spectra and the HPLC profile of the extracts are shown in Figures 2a, 3a, and 4a, respectively. After removal of TCB from the extract, the residue was dissolved in ODCB and reduced at a controlled potential of 0.00 V vs SCE as indicated before. A vis-NIR spectrum of the resulting solution showed an absorption maximum at 934 nm characteristic of [La@C₈₂-A][−].

The ODCB was removed by evaporation, and the residue was extracted by acetone/CS₂ (=4:1). The precipitate was collected by filtration and extracted with CS₂. Figures 2b and 4b show the LD-TOF mass spectrum and the HPLC profile of the CS₂ solution (sample

(13) Wakahara, T.; Okubo, S.; Kondo, M.; Maeda, Y.; Akasaka, T.; Waelchli, M.; Kako, M.; Kobayashi, K.; Nagase, S.; Kato, T.; Yamamoto, K.; Gao, X.; Caemelbecke, E. V.; Kadish, K. M. *Chem. Phys. Lett.* **2002**, *360*, 235.

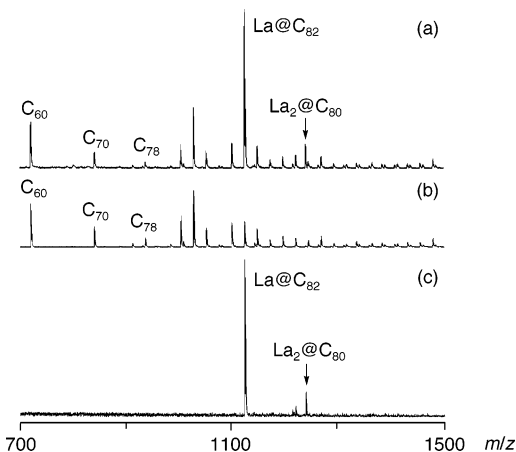


Figure 2. Positive ion laser desorption mass spectra of (a) TCB extracts of raw soot, (b) sample 1, and (c) sample 3 in Scheme 2.

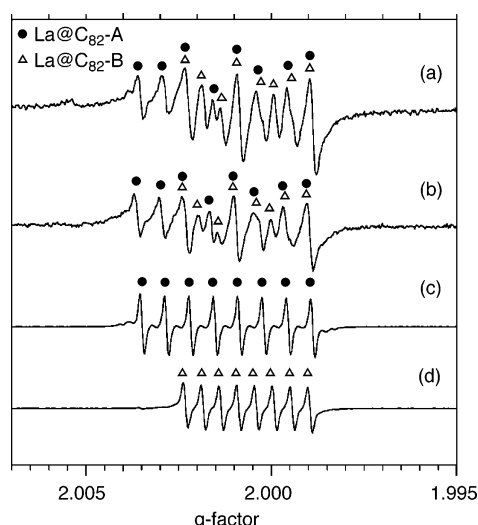


Figure 3. ESR spectra of (a) TCB extracts from soot, (b) sample 3 in Scheme 2, (c) $\text{La@C}_{82}\text{-A}$, and (d) $\text{La@C}_{82}\text{-B}$ purified by preparative HPLC.

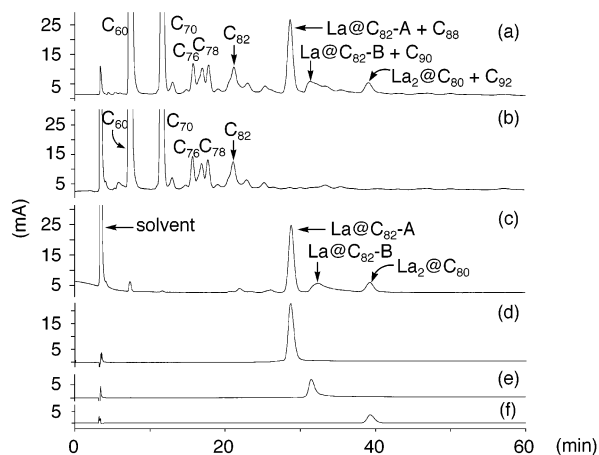


Figure 4. HPLC profiles for (a) TCB extracts, (b) sample 3 in Scheme 2, and (c) $\text{La@C}_{82}\text{-A}$, (d) $\text{La@C}_{82}\text{-B}$, and (e) $\text{La}_2\text{@C}_{80}$ isolated [Buckeyprep column (ϕ 4.6 \times 250 mm), toluene as eluent, flow rate: 1 mL/min, 40 $^{\circ}\text{C}$]. The volume of those samples and the injection volumes were aligned.

1), respectively. As can be seen in Figures 2b and 4b, both La@C_{82} and $\text{La}_2\text{@C}_{80}$ have been removed as compared to what is seen in Figures 2a and 4a. On the other

hand, a vis-NIR spectrum of the acetone/ CS_2 solution (sample 2) shows an absorption maximum for $[\text{La@C}_{82}\text{-A}]^-$ at 934 nm. An LD-TOF mass spectrum of sample 2 suggests that the empty fullerenes were eliminated and that La@C_{82} and $\text{La}_2\text{@C}_{80}$ were concentrated in the acetone/ CS_2 solution.

The oxidation of endohedral metallofullerene anions to their neutral forms by the weak acid CHCl_2COOH was examined.¹¹ Addition of CHCl_2COOH to the acetone/ CS_2 solution led to precipitation of a dark brown solid, which could be extracted with CS_2 . A vis-NIR spectrum of the CS_2 solution of the precipitate (sample 3) shows an absorption maximum at 1010 nm characteristic of La@C_{82} . Its LD-TOF mass spectrum (shown in Figure 2c) was almost the same as that in sample 2. The ESR spectrum of sample 3 showed octet signals, which correspond to $\text{La@C}_{82}\text{-A}$ and $\text{La@C}_{82}\text{-B}$, as shown in Figure 3b. These results indicate that electrochemically reduced endohedral metallofullerenes can be converted back to their neutral forms by oxidation with CHCl_2COOH . Figure 4c shows an HPLC profile of sample 3 in which the empty fullerenes are almost undetectable. $\text{La@C}_{82}\text{-A}$, $\text{La@C}_{82}\text{-B}$, and $\text{La}_2\text{@C}_{80}$ can be easily isolated following a one-stage HPLC separation of the sample.

By using the above-described purification technique, we could obtain much larger amounts of pure $\text{La@C}_{82}\text{-A}$, $\text{La@C}_{82}\text{-B}$, and $\text{La}_2\text{@C}_{80}$ than the HPLC purification method previously used to isolate these compounds from extracts.⁴ A small production is undesirable in that it slows progress for developing further applications. Thus, a most effective method to purify $\text{La@C}_{82}\text{-A}$ has been developed; previously, it has taken about 1 week to get 10 mg of purified $\text{La@C}_{82}\text{-A}$, but it now takes only 1 day to get the same amount of $\text{La@C}_{82}\text{-A}$. Therefore, it is now possible to obtain $\text{La@C}_{82}\text{-A}$ in large quantities. The successful isolation of endohedral metallofullerenes in microscopic amounts by using this method is an important stepping-stone on the way to developing future materials, as well as catalytic and biological applications using these materials.

Conclusion

A selective electrochemical reduction of the endohedral metallofullerenes from extracts of carbon soot and a development of a convenient separation method of endohedral metallofullerenes and empty fullerenes are accomplished. A chemical oxidation of the endohedral metallofullerene anions is also discussed.

Experimental Section

The reagents acetone, toluene, 1,2,4-trichlorobenzene (TCB), carbon disulfide, and $n\text{-Bu}_4\text{NClO}_4$ were obtained commercially and used as received. *o*-Dichlorobenzene (ODCB) was dried by distillation from P_2O_5 under reduced pressure prior to use.

Soot containing metallofullerenes was produced by the standard arc vaporization method with a ϕ 4.6 \times 130 mm composite anode containing graphite and lanthanum oxide in an atomic ratio of $\text{La/C} \approx 0.008$. The composite rod was then subjected to an arc discharge as an anode under a helium atmosphere of 100 Torr. The raw soot (~ 2 g) was collected and extracted with 60 mL of TCB at its boiling temperature for 15 h under argon atmosphere. The resultant solution was thoroughly filtered off with 20 mL of TCB, and the solvent was evaporated on a rotary evaporator. Bulk controlled-potential

electrolysis of the extracts in 25 mL of ODCB containing 0.03 M $n\text{-Bu}_4\text{NClO}_4$ at 0.00 V vs SCE was used to prepare the endohedral metallofullerene anions with a potentiostat/galvanostat (BAS CW-50). After the electrolysis, the ODCB was removed by evaporation, and the precipitate was washed with 50 mL of acetone/ CS_2 (=4:1) to extract endohedral metallofullerene anions. The resulting residue was extracted with 50 mL of CS_2 . Addition of 5 mg of CHCl_2COOH to the acetone/ CS_2 solution yielded neutral endohedral metallofullerenes as a dark brown solid, which could be extracted with 50 mL of CS_2 . The CS_2 solution of neutral endohedral metallofullerenes was replaced to 25 mL of toluene solution, and it was injected into the HPLC with PYE column (ϕ 20 \times 250 mm, eluent: toluene, flow rate: 10 mL/min). After one-stage HPLC separation, 2.0, 1.5, and 1.9 mg of pure $\text{La@C}_{82}\text{-A}$, $\text{La@C}_{82}\text{-B}$, and $\text{La}_2\text{@C}_{80}$ were isolated, respectively.

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Supporting Information Available: The LD-TOF mass and UV spectral data of isolated $\text{La@C}_{82}\text{-A}$, $\text{La@C}_{82}\text{-B}$, and $\text{La}_2\text{@C}_{80}$ (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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