JOURNAL OF Materials CHEMISTRY

Novel proficient method for isolation of endometallofullerenes from fullerene-containing soots by two-step *o*-xylene–*N*,*N*-dimethylformamide extraction

Elena E. Laukhina,[a] Vyacheslav P. Bubnov,[a] Yakov I. Estrin,[a] Yurii A. Golod,[b] Mikhail A. Khodorkovskii,[b] Vitali K. Koltover[a] and Eduard B. Yagubskii*[a]†

[a]*Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences, Chernogolovka, 142432, Moscow Region, Russia*
[b]*State Institute of Applied Chemistry, S.-Petersburg, Russia*

We have developed a novel proficient method of extraction of endohedral metallofullerenes from fullerene-containing soots. The method consists of two extraction steps. In the first step, *o*-xylene is used to extract empty fullerenes from the soot. In the second step, the same soot is extracted by polar solvent *N*,*N*-dimethylformamide. This method has been applied for isolation of endohedral La- and Y-fullerenes from the soots obtained in the electric-arc reactor. The resultant DMF extracts contain virtually no C_{60}, C_{70} or other empty fullerenes. The yield of the DMF extracts reaches 1% of the primary soot mass. The simple extraction method developed here enables production of large amounts of concentrated $M@C_{2n}$.

Endometallofullerenes (incarceranes, $M@C_{2n}$) are endohedral carbon clusters that contain metal atoms (lanthanides, or Sc, Y, U and Ca) trapped within a fullerene cage.[1] The unique structure and reactivity of $M@C_{2n}$ are of great interest in the context of their chemical reactivity and their prospects as new molecular magnets, metals and superconductors.[1–11] It has been suggested that $La@C_{82}$ can be used for measurement of oxygen in microheterogeneous chemical and biological systems.[12] However, physical and chemical properties of $M@C_{2n}$ are as yet poorly investigated owing to their poor accessibility. Fullerene-containing soots, produced in an electric-arc reactor or by the laser vaporisation technique, normally contain no more than 0.1% $M@C_{2n}$. It is the usual practice to perform extraction of $M@C_{2n}$ from the soots in one step with the help of conventional solvents, such as CS_2 or toluene, formerly used for extraction of empty fullerenes.[1–5] Since these solvents do not have any selectivity to endometallofullerenes, the empty fullerenes (C_{60}, C_{70}, *etc.*) are about two orders of magnitude more abundant than $M@C_{2n}$ in the resultant extracts. Further isolation of $M@C_{2n}$ from these extracts by HPLC is a laborious procedure, consuming much time and cost, and only milligram quantities of $M@C_{2n}$ of 96–98% purity are currently available (see, *e.g.*, ref. 4). Therefore, improvement in methods for the synthesis and isolation of $M@C_{2n}$ is one of the current problems in the area of chemistry and physics of carbon clusters.

As far as the $M@C_{2n}$ molecules have essentially asymmetrical electron structures[4] they should possess large dipole moments in contrast to empty fullerene molecules. Fuchs *et al.* have found that the amount of $La@C_{82}$ in the extract was 2–3 times higher when a relatively polar azeotrope CS_2–MeOH was used as the extraction solvent instead of pure CS_2.[6] By use of DMF with its large dipole moment (3.82 D) and a one-step extraction method, Ding and Yang obtained extracts containing 5–15% endohedral metallofullerenes ($Ce@C_{82}$).[7] However, the total yield of $M@C_{2n}$ after the one-step DMF extraction did not exceed 0.1% of the mass of the primary soot.[7]

In our previous paper we showed that *o*-xylene serves as an effective solvent for extraction of empty fullerenes from endometallofullerene-containing soots.[9] Here, we show that a simple two-step extraction scheme with *o*-xylene as the first solvent and DMF as the second solvent makes it possible to produce large quantities of $M@C_{2n}$ with the absence of empty fullerenes.

Experimental

Endometallofullerene-containing soots were synthesised in an electric-arc reactor, the design of which had been described in our previous papers.[9,13] The graphite electrodes were composed with elemental lanthanum or yttrium. The conditions of evaporation of the electrodes in the arc were as follows: helium pressure 120 Torr, direct current 90 A, voltage 28–30 V, arc length 5 mm, distance between the arc and the cooled wall of the reactor 50 mm, evaporation rate 1 mm min^{-1}.[9] The soot was collected from the reactor walls and kept in a desiccator under vacuum. The solvents, *o*-xylene and DMF, were preliminarily dried, distilled, deoxygenated by streaming with argon, and stored in an atmosphere of argon.

Endometallofullerenes $M@C_{2n}$ were extracted from the fullerene-containing soots under argon according to the two-step scheme: *o*-xylene–DMF. In the first step, the soot was treated with *o*-xylene. A weighed sample of the soot (10 g) was placed in a filter-paper vessel that, in its turn, was placed in a glass flask containing 250 ml of *o*-xylene. The extraction procedure was continued for 3 h at the boiling point of the solvent under argon. The solution of fullerenes was thoroughly filtered off, the solvent was evaporated on a rotary evaporator and the extract was dried for 1 h at 90 °C *in vacuo*. The soot sample was treated several more times following the same procedure, until the next fresh solvent portion was virtually colourless. This colourless fraction of *o*-xylene served as a performance criterion to end the first step of the soot extraction. After the first extraction step, 0.13 g of fullerene extract was produced. This *o*-xylene extract (yield 1.3%) contained C_{60} (*ca.* 78%), C_{70} (*ca.* 20%) and $La@C_{82}$ (*ca.* 0.5%).

Once the soot has been treated with *o*-xylene (usually, three cycles), it was then put through the second extraction step with DMF. The extraction was performed in analogous fashion in 250 ml DMF during 3 h (one cycle). After evaporation of the solvent, the residue was dried for 1 h at 90 °C *in vacuo.* 0.1 g of the DMF extract was isolated which accounted for 1% of the primary soot sample. All extracts were stored under argon.

---

† E-mail: yagubski@icp.ac.ru

Endometallofullerenes were identified by mass spectrometry, optical spectrophotometry and EPR spectroscopy. The mass spectrometric analysis was performed by a matrix-assisted laser-desorption ionisation (MALDI) technique, using a time-of-flight mass spectrometer (TOF-1, Bruker). The measurements were carried out with cinnamic acid as the matrix and also in its absence using laser pulses of different wavelengths (240–260 nm) and of 15 ns duration. UV–VIS spectra were recorded in the range 300–1100 nm on an HP-8453 spectrometer (Hewlett-Packard). IR spectra were recorded on a Specord-M82 spectrometer (Karl Zeiss, Jena) using the KBr pellet technique. EPR spectra were recorded on a Varian E-104A radiospectrometer (USA) in the X-range (9 GHz) at *ca.* 20 °C. The samples for EPR measurements were prepared as solutions in standard quartz tubes with an inner diameter of 3 mm. The samples were thoroughly deoxygenated by multiple freezing–thaw cycles before the tubes were sealed *in vacuo*. The elemental content in the extracts was determined by X-ray fluorescence analysis on a VRA-30 analyser (Germany) and by the standard technique of elemental microanalysis.

Results

Fig. 1 shows a MALDI mass spectrum of a DMF extract from La@C$_{2n}$-containing soots. The mass spectrum, obtained with cinnamic acid as the matrix, exhibits a large number of lines in the range of molecular masses from *m*/*z* 1027 to 1411 which correspond to molecular ions from La@C$_{74}^+$ to La@C$_{106}^+$. However, there are virtually no peaks of empty fullerenes (C$_{60}$, C$_{70}$ or higher) in this mass spectrum. The absence of empty fullerenes in the DMF extract has also been confirmed by HPLC. The most intense peak in the mass spectrum belongs to La@C$_{82}^+$ while the peaks corresponding to other M@C$_{2n}$ are of lower intensity (Fig. 1 and Table 1). In the absence of matrix, the same specimen displayed a mass spectrum in which the lines of La@C$_{76}^+$ and La@C$_{78}^+$ were of almost the same intensity as the dominant line of La@C$_{82}^+$. This change in intensity is obviously caused by fragmentation of La@C$_{82}$ in the laser beam with the formation of additional amounts of low-mass M@C$_{2n}$. Such fragmentation does not seem to take place under the milder conditions of laser desorption and ionisation in the presence of the matrix.

Fig. 2 shows a UV–VIS spectrum of the DMF extract in *o*-dichlorobenzene. This spectrum displays two broad absorption bands at 1000 and 840 nm, the first of which is typical for La@C$_{82}$ while the second band can probably be ascribed to La@C$_{80}$. Absorption bands in the range 300–500 nm characteristic of empty fullerenes (C$_{60}$, C$_{70}$) are essentially absent.

Furthermore, it has been shown by X-ray fluorescence analysis that the content of La in the DMF extract is 12.3±0.2%. This result is in accordance with the theoretical content of La in La@C$_{82}$ (12.36%) and in La@C$_{80}$ (12.63%) and verifies that La@C$_{2n}$ endometallofullerenes have been concentrated to nearly 100% in the DMF extract.

Table 1 Molecular masses and relative abundance (RA) of metallofullerenes La@C$_{2n}$ ($2n = 74$–106) in the DMF extract

La@C$_{2n}$	*M* (*m*/*z*)	RA(%)
La@C$_{74}$	1028	9.5
La@C$_{76}$	1052	16.5
La@C$_{78}$	1076	18.2
La@C$_{80}$	1100	53.9
La@C$_{82}$	1124	100
La@C$_{84}$	1148	11.3
La@C$_{86}$	1172	13
La@C$_{88}$	1196	7.8
La@C$_{90}$	1220	17.4
La@C$_{92}$	1244	7.8
La@C$_{94}$	1268	6.9
La@C$_{96}$	1292	5.2
La@C$_{98}$	1316	7.8
La@C$_{100}$	1340	6.9
La@C$_{102}$	1364	10.4
La@C$_{104}$	1388	9.0
La@C$_{106}$	1412	12.2

Fig. 3 shows the EPR spectra of the DMF extracts. The spectrum of the DMF extract dissolved in *o*-dichlorobenzene displays two octets, each consisting of eight narrow lines of approximately equal intensity [Fig. 3(*a*)]. For the first octet the hyperfine splitting constant, $a = 1.15 \pm 0.03$ G. The second signal is characterised by $a = 0.81 \pm 0.04$ G and the octet signals partially overlap. For example, the fifth and seventh components of the first octet superimpose, respectively, the fourth and seventh components of the second. Both octet signals are similar to the EPR signals of two different isomers of La@C$_{82}$ that have been described previously.[1–3,9,12] The hyperfine patterns of these spectra are caused by the interaction of the unpaired electron with the spin moment of the lanthanum nucleus ($I = 7/2$) with <1% of the unpaired spin density being localized at the lanthanum while the remainder is distributed over the carbon atoms of the fullerene shell.[1–3] Along with the lines of two main octets, weak lines due to the presence of small amounts of other La@C$_{2n}$ and the lines of the hyperfine structure on ^{13}C also contribute to the total intensity.

The EPR spectrum of the DMF extract in DMF solution is

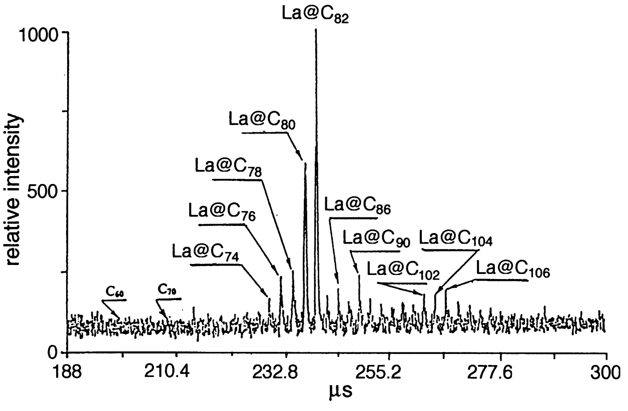

Fig. 1 Matrix-assisted (MALDI) mass spectrum of the DMF extract from the La@C$_{2n}$-containing soot

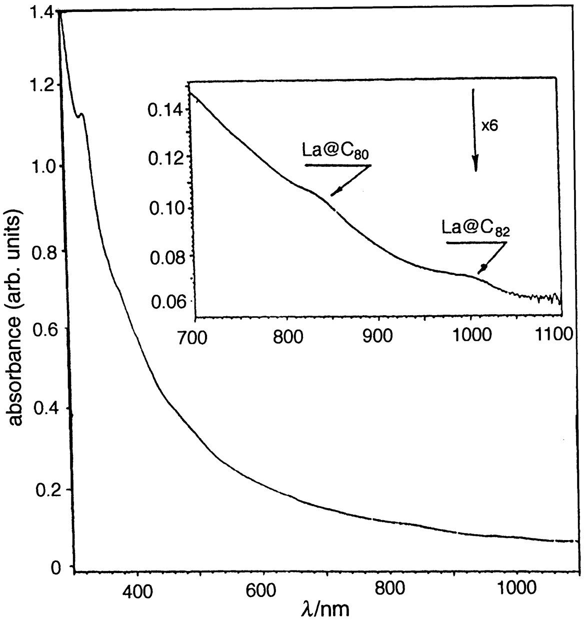

Fig. 2 UV–VIS absorption spectrum of the DMF extract from the La@C$_{2n}$-containing soot in *o*-dichlorobenzene

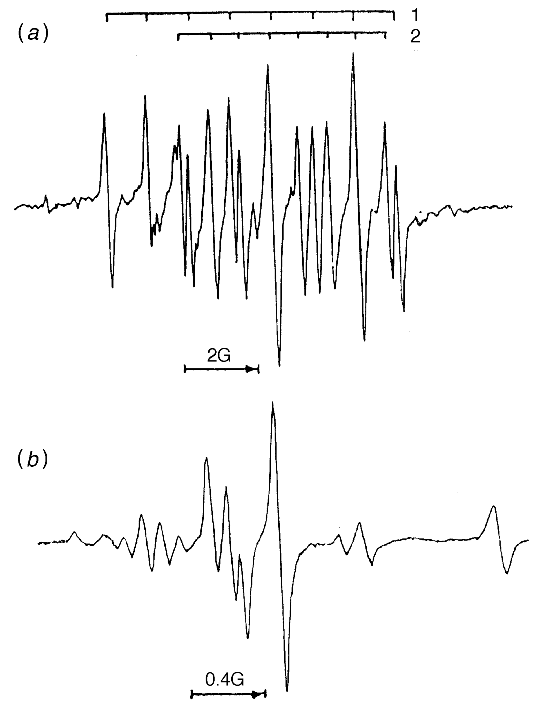

Fig. 3 EPR spectra of the DMF extract from the La@C_{2n}-containing soot in *o*-dichlorobenzene (*a*) and in DMF (*b*). Conditions: room temperature; frequency and amplitude of the magnetic field modulation 100 kHz and 0.025 G; microwave power 1 mW (*a*) or 0.5 mW (*b*); sweep rate 1.25 G min^{-1} (*a*) or 0.25 G min^{-1} (*b*); time constant 0.250 s (*a*) or 0.128 s (*b*); receiver gain $1.6 \times 10^3 \times 10$ (*a*) or $2.0 \times 10^2 \times 10$ (*b*). The spectra were recorded in the absence of oxygen.

different from the EPR spectrum of the same specimen in *o*-dichlorobenzene [Fig. 3(*b*)]. Although the origin of this spectrum calls for further investigation, the triplet signal with $a \approx 0.1$ G may be assigned to the hyperfine interaction of the unpaired electron of La@C_{82} with the nuclear spin of ^{14}N ($I = 1$) of DMF.

Elemental analysis showed that the DMF extract contains nitrogen (2.2%) and hydrogen in addition to carbon and lanthanum. The IR spectrum of the DMF extract showed the absorption bands arising from the stretching vibrations (2925 and 2854 cm^{-1}) and from the deformation vibrations (1387 cm^{-1}) of the methyl groups of DMF along with a band at 1652 cm^{-1} arising from the stretching vibrations of the carbonyl group of DMF. The latter was displaced by 20 cm^{-1} to lower frequency compared to pure DMF (1652 *vs.* 1672 cm^{-1}). This shift may be due to an interaction between DMF and La@C_{2n}.

We also employed the same two-step *o*-xylene/DMF extraction scheme for isolation of yttrium endohedral metallofullerenes. On evidence derived from the mass spectra, there were practically no empty fullerenes in the DMF extract from Y@C_{2n}-containing soot. As for La, the yield of Y@C_{2n} was *ca.* 1% of the primary soot.

Discussion

The advantage of the procedure described here lies in usage of two consecutive extraction steps, each relying on a fundamental difference in polarity between endohedral metallofullerenes and empty fullerenes. In the first step, *o*-xylene was used. This solvent of low polarity expelled empty fullerenes from the fullerene-containing soot but did not significantly reduce the content of M@C_{2n} in the soot.[9] In the second step, DMF was employed for the selective extraction of M@C_{2n} from the residue soot.

Recently a two-step procedure for the extraction of Ce@C_{2n} was used in ref. 8. After having extracted a soot with toluene in a Soxhlet extraction apparatus, the authors extracted the remaining soot by use of pyridine and a high-temperature, high-pressure extraction technique. The resultant pyridine extract contained up to 75% of Ce@C_{2n} and its yield accounted for 0.6% of the primary soot. However, it should be noted that while performing the high-pressure pyridine extraction, these authors could only work with very small amounts of soot (10 mg). By contrast, we obtained as much as 100 mg of the endometallofullerene concentrate upon extraction of 10 g of the primary soot.

Thus, the simple extraction scheme, described here, has afforded, for the first time, production of endohedral metallofullerenes in large preparative amounts.

The authors are indebted to Dr. V. P. Ladygina for performing IR spectroscopy measurements and to Dr. O. L. Lependina for the X-ray fluorescence analysis. Yu. A. G. and M. A. Kh. are grateful to The United Research Center of S.-Petersburg for the help with the mass spectrometry measurements. This contribution was supported by Russian State Scientific Technical Program 'Current Directions in Condensed Matter Physics', sub-program 'Fullerenes and Atomic Clusters'.

References

1 D. S. Bethune, R. D. Johnson, J. R. Salem, M. S. de Vries and C. S. Yannoni, *Nature (London)*, 1993, **366**, 123.
2 K. Kikuchi, Y. Nakao, S. Suzuki and Y. Achiba, *J. Am. Chem. Soc.*, 1994, **116**, 9367.
3 L. Dunsch, A. Bartl, U. Kirbach and J. Frohner, in *Fullerenes (Proc. Symp. Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials)*, ed. R. S. Ruoff and K. M. Kadish, The Electrochem. Soc., Pennington, NJ, 1995, p. 182.
4 S. Nagase, K. Kobayashi and T. Acasaka, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 2131.
5 Z. D. Xu, T. Nakane and H. Shinohara, *J. Am. Chem. Soc.*, 1996, **118**, 11 309.
6 D. Fuchs, H. Rietschel, R. H. Michel, A. Fischer, P. Weis and M. M. Kappes, *J. Phys. Chem.*, 1996, **100**, 725.
7 (*a*) J. Q. Ding and S. H. Yang, *Chem. Mater.*, 1996, **8**, 2824; (*b*) J. Q. Ding and S. H. Yang, *J. Am. Chem. Soc.*, 1996, **118**, 11 254.
8 D. Y. Sun, Z. Y. Liu, X. H. Guo, W. G. Xu and S. Y. Liu, *J. Phys. Chem. B*, 1997, **101**, 3927.
9 V. P. Bubnov, V. K. Koltover, E. E. Laukhina, Ya. I. Estrin and E. B. Yagubskii, *Russ. Chem. Bull.*, 1997, **46**, 254.
10 B. L. Tumanskii, V. V. Bashilov, S. P. Solodovnikov, B. I. Sokolov, V. P. Bubnov, E. E. Laukhina, Ya. I. Estrin, V. K. Koltover and E. B. Yagubskii, *Fullerene Sci. Technol.*, 1998, **6**, No. 3.
11 M. S. Dresselhaus, *Sci. Spectra*, 1997, **7**, 36.
12 V. K. Koltover, E. E. Laukhina, Ya. I. Estrin, V. P. Bubnov and E. B. Yagubskii, *Proc. Russ. Acad. Sci. (Dokl. Phys. Chem.)*, 1997, **353**, 57.
13 V. P. Bubnov, I. S. Krainskii, E. E. Laukhina and E. B. Yagubskii, *Russ. Chem. Bull.*, 1994, **43**, 805.

Paper 7/08385E; *Received* 20*th November*, 1997