Selective Extraction of Endohedral Metallofullerenes Using a Mixed Solvent of Triethylamine and Acetone

Takeshi Kodama,* Korenari Higashi, Takafumi Ichikawa, Shinzo Suzuki, Hiroyuki Nishikawa,
Isao Ikemoto, Koichi Kikuchi, and Yohji Achiba
Department of Chemistry, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397

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We have developed a single-step method for selectively extracting endohedral metallofullerenes. In this new method, a mixed solvent of triethylamine and acetone is used to extract endohedral metallofullerenes from raw soot. The efficiency of extraction was investigated by extracting Ce-containing metallofullerenes, Ce@C_{82} and Ce_2@C_{80}, from raw soot obtained by an arc discharge technique. The resultant extract contained little or no empty fullerenes such as C_{60} or C_{70}, that is, the Ce-metallofullerenes were selectively extracted.

Endohedral metallofullerenes have long attracted wide interest not only in physics and chemistry, but also in the material and biological sciences.[1,2] However, the preparation of macroscopic amounts of pure endohedral metallofullerenes is still a time-consuming process, and this prevents researchers from studying endohedral metallofullerenes in a wider scientific area. One of the reasons for the difficulty is that empty fullerenes, mainly C_{60}, are about two orders of magnitude more abundant than endohedral metallofullerenes in extracts from raw soot. Therefore, multistep chromatographic procedures, which are time and solvent consuming, are indispensable for the isolation of endohedral metallofullerenes.

One way to overcome the difficulty is to enhance the extraction efficiency of endohedral metallofullerenes. So far, organic solvents such as toluene, carbon disulfide, 1,2,4-trichlorobenzene, *N*,*N*-dimethylformamide (DMF), and pyridine have been used to extract endohedral metallofullerenes; in particular, extraction using DMF[3] and pyridine[4] is rather effective to select metallofullerenes. Recently, selective extraction methods by chemical oxidation,[5–7] chemical reduction,[8] or electrochemical reduction[9] have been developed. However, each method, except for those reported in refs 7 and 8, requires sublimation and/or pre-extraction with the usual organic solvents; namely, a multi-step process is required for selective extraction. In refs 7 or 8, direct extraction of endohedral metallofullerenes from raw soot was tried by chemical oxidation[7] or chemical redutcion,[8] but their extraction efficiency of endohedral metallofullerenes is considered not so high.

In this study, we assumed that the efficiency of extraction for endohedral metallofullerenes by DMF and pyridine comes from their donicity, so we used triethylamine (TEA) in the expectation that it would act as a more effective donor. TEA was mixed with acetone to suppress the extraction of empty fullerenes such as C_{60}. Here, we report on a single-step process for the selective extraction of endohedral metallofullerenes, using Ce-metallofullerenes as an example, employing a mixed solvent of triethylamine and acetone.

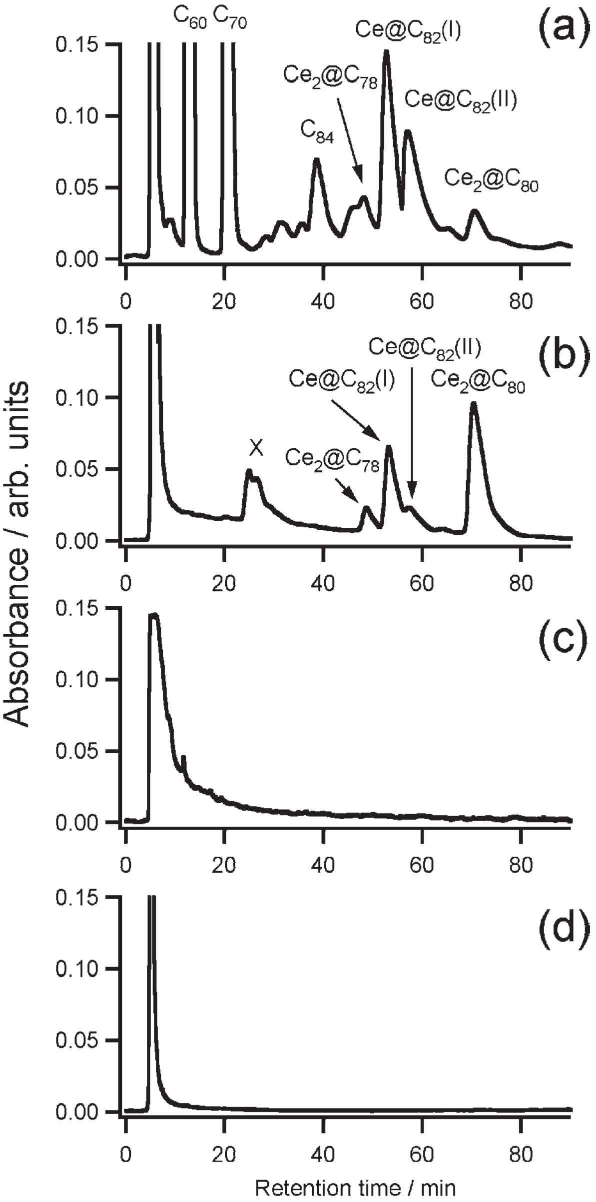

Figure 1. HPLC chromatograms of (a) TCB, (b) mixed solvent (TEA/acetone), (c) TEA, and (d) acetone extracts from raw soot produced by arc discharge of Ce/C composite rods.

Raw soot containing Ce-metallofullerenes was produced by direct current (70 A) arc discharge of Ce/C composite rods (Toyo Tanso Co. Ltd., 8 × 8 × 100 mm, 2 atom %) in a 500 Torr He atmosphere. The raw soot obtained was divided into four parts and each part was extracted using a different solvent, either

1,2,4-trichlorobenzene (TCB) (400 mL), TEA/acetone (100 mL/300 mL), TEA (400 mL), or acetone (400 mL). Extraction was continued for 6 h at the boiling point of each solvent. The extracted solution was filtered through a membrane filter, and was vacuum-evaporated to remove the solvent. The soluble fraction was dissolved in toluene and injected into a preparative HPLC with a COSMOSIL Buckyprep column (20 mm $\phi \times$ 250 mm, Nacalai Tesque). The mobile phase was toluene and the elution rate was 12 mL/min. The elution behavior was monitored by UV absorption at 340 nm, and the gain of the UV detector was unchanged for all the extracts to compare the extraction yields of Ce-metallofullerenes directly.

Figure 1a shows an HPLC chromatogram of the TCB extract. The most abundant fullerene is C_{60}, and the next is C_{70}. The peak intensities of two $Ce@C_{82}$ isomers are significantly higher than that of C_{84}, and the distinct peak of $Ce_2@C_{80}$ is also clearly seen. These observations indicate that the raw soot obtained in the present arc discharge contained Ce-metallofullerenes with a rather high production yield.

Figure 1b is an HPLC chromatogram of the mixed solvent (TEA/acetone) extract. Surprisingly, $Ce_2@C_{80}$ is the most abundant, and $Ce@C_{82}$ is next. Little or no empty fullerenes such as C_{60} and C_{70} are present. The fraction marked with X was found to contain $Ce@C_{82}$ and $Ce_2@C_{80}$ by LD-TOF-MS. However, the elution behavior of this fraction is clearly different from normal $Ce@C_{82}$ and $Ce_2@C_{80}$, which are eluted much later. Therefore, they are tentatively assigned as derivatives of $Ce@C_{82}$ and $Ce_2@C_{80}$, which cannot be confirmed by LD-TOF-MS because of fragmentation due to laser ionization.

To check whether or not mixing two solvents is essential for selective extraction of metallofullerenes, we tried to extract fullerenes from the raw soot with just TEA or with acetone only. The result is that neither empty fullerenes nor Ce-metallofullerenes are present in the TEA extract or in the acetone extract as shown in Figures 1c and 1d. Therefore, mixing two solvents is found to be the key factor for selective extraction of metallofullerenes.

Table 1. HPLC peak intensities of Ce-metallofullerenes[a]

	$Ce_2@C_{80}$	$Ce@C_{82}$(I)	$Ce@C_{82}$(II)
TCB extract	0.025	0.137	0.082
TEA/acetone extract	0.091	0.059	0.017

[a]Baseline correction was done.

Why is mixing two solvents so important? The peak intensities of three kinds of Ce-metallofullerenes, $Ce_2@C_{80}$, $Ce@C_{82}$(I), and $Ce@C_{82}$(II), in Figures 1a and 1b are summarized at Table 1. Because the peak of $Ce_2@C_{78}$ significantly overlaps with that of empty fullerenes, mainly C_{86}, the peak intensity of $Ce_2@C_{78}$ itself could not be estimated. Therefore, $Ce_2@C_{78}$ is excluded from the discussion. The extraction yield of $Ce_2@C_{80}$ with TEA/acetone is considerably much higher than that with TCB. In contrast to $Ce_2@C_{80}$, the extraction yield of $Ce@C_{82}$ with TEA/acetone is somewhat lower than that with TCB, moreover, the yield of $Ce@C_{82}$(II) is much less compared to that of $Ce@C_{82}$(I). The order of the extraction yields with TEA/acetone for the three Ce-metallofullerenes, $Ce_2@C_{80}$, $Ce@C_{82}$(I), and $Ce@C_{82}$(II), corresponds to that of the first reduction potentials of La-metallofullerene analogues, $La_2@C_{80}$, $La@C_{82}$-A, and $La@C_{82}$-B, whose first reduction potentials are -0.31, -0.42, and -0.47 (V vs Fc/Fc^+),[10] respectively. Therefore, we propose the following process for the selective extraction of metallofullerenes with TEA/acetone. First, because TEA is a substantially strong electron donor with a donor number of 61,[11] TEA reduces a metallofullerene to its anion or forms a donor–acceptor complex (D–A complex) with the metallofullerene. On the other hand, the first reduction potentials of empty fullerenes are rather large (e.g. -1.12 V vs Fc/Fc^+ for C_{60});[10] therefore, they are hardly reduced by TEA or form D–A complexes with TEA and so remain neutral. Secondly, the resulting anion or D–A complex is solvated by the polar solvent, acetone, and is extracted. The efficiency of the reduction or formation of the D–A complex should depend on the first reduction potentials of the metallofullerenes; therefore, this series of events explains the order of the efficiency of the extraction. A spectroscopic study for confirming the reduction or D–A complex formation with TEA is now in progress.

In conclusion, we have achieved the selective extraction of metallofullerenes using a mixed solvent of TEA/acetone.

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