Isolation and characterization of higher metallofullerenes Ca@C$_{92}$ and Ca@C$_{94}$

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Abstract. We report for the first time isolation of Ca@C$_{92}$ and Ca@C$_{94}$ by multi-stage high-performance liquid chromatography technique without recycling equipment. It is notable that higher metallofullerenes containing alkaline earth metal ions could be isolated although their relative yields are extremely low. Ca@C$_{92}$ and Ca@C$_{94}$ are also confirmed by LD-TOF mass spectrometry and characterized by UV-Vis-NIR absorption measurements.

Keywords. HPLC; Metallofullerenes; LD-TOF-MS; UV-Vis-NIR absorption.

1. Introduction

Endohedral metallofullerenes have attracted much attention because of their unique structures, novel properties[1] and promising applications in biology and advanced materials. In 1991, Chai *et al* reported the first macroscopic amount of metallofullerenes by laser vapourization of a graphite–metal composite in a helium filled tube oven at high temperature.[2] Subsequently, effort was made in production, isolation and characterization of endohedral metallofullerenes, mostly based on C$_{82}$ and C$_{84}$ encapsulating trivalent elements[1] such as La, Gd, Tb, Sc and Y. However, investigations on divalent metallofullerenes containing Sm, Eu, Yb, Ca, Sr and Ba are severely limited, especially for higher ones with extremely low yields,[3–5] of which Yb@C$_{94}$ and Ca@C$_{90}$ is the largest cage size for lanthanide and alkaline earth higher metallofullerenes isolated and characterized, respectively, till now.

For divalent metallofullerenes, progresses in the two main parallel and important research fields provide with valuable information such as ultraviolet-visible-near infrared (UV-Vis-NIR) or ^{13}C Nuclear Magnetic Resonance (NMR) characterization in common indicating their similar molecular symmetry and charge population between the cage and the encapsulated metal ions.

Unlike the relevant smaller Eu, Yb and Ca endohedral fullerenes with C$_{2n}$ ($36 \leq n \leq 44$) cages, the two isomers of Yb@C$_{90}$[6] are quite different from Eu@C$_{90}$[7] and the two isomers of Ca@C$_{90}$[8] according to their UV-Vis-NIR absorption spectra. So it is meaningful to synthesize and isolate Ca@C$_{92}$ and Ca@C$_{94}$ to enlighten the formation mechanism of higher endohedral fullerenes and evaluate the effects of perturbation on the cages from different elements included. Furthermore, the constant +2 oxidation state of Ca in Ca@C$_{92}$ and Ca@C$_{94}$ can be an indicator of the electrical valence of the encapsulated Yb ions on condition that they possess close similarly UV-Vis-NIR absorption spectra. After all, no direct ultraviolet photoelectron spectroscopy (UPS), X-ray photoelectron spectroscopy (XPS) or electron energy loss spectroscopy (EELS) observation of valence state of lanthanide elements for their endohedral fullerenes higher than C$_{84}$ cage size has been reported up to date. So research work in Ca endohedral fullerenes is of significance.

Although the yields of Ca-metallofullerenes are even lower than that of Sm, Eu, Yb or Tm, we succeeded in synthesis, isolation and characterization of Ca@C$_{92}$ and Ca@C$_{94}$ for the first time. The *o*-dichlorobenzene extraction, chlorobenzene and benzene mobile phase for isolation of fullerenes and endohedral fullerenes in our work had never been reported before.

2. Experimental

Our raw soot containing Ca metallofullerenes was produced by an optimized direct current arc (DC)

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discharge method[9] and then ultrasonicated in *o*-dichlorobenzene solvent for 3 h keeping around 45°C. The isolation process was carried out by multi-stage high-performance liquid chromatography (HPLC). Three complementary columns: Buckyprep column, 5-PBB column and Buckyprep-M column ($\phi 10 \times 250$ mm Nacalai Tesque) were used. The purities of isomer free species were confirmed > 98% by laser desorption time-of-flight mass spectrometry (LD-TOF-MS)(EXPLORER 4700, A&B Inc.). Their UV-Vis-NIR spectra were measured by U4100 spectrophotometer (Hitachi High-Technologies Corporation) in benzene solution.

The *o*-dichlorobenzene solvent can dissolve fullerenes or metallofullerenes from raw soot more efficiently with a solubility of C_{60} five times that of *o*-xylene and three times of 1,2,4-trichlorobenzene. The *o*-dichlorobenzene extractant was removed into chlorobenzene for the first step of rough separation that was carried out on semipreparative Buckyprep-M column with chlorobenzene eluent. Fraction 1 (F1) retented from 10·7 to 12·7 min was collected (figure 1a). The main purpose of this most time consuming stage is to remove abundant hollow small cage fullerenes and enrich higher metallofullerenes at the same time. Strong polarity and dissolving power of chlorobenzene mobile phase greatly shortened the retention time, decreased the whole injection volume, and improved the isolation efficiency nearly four times compared to the prevalent toluene eluent. Obviously, the higher viscosity of aniline and low boiling point with strong nerve toxicity of carbon bisulfide made them not suitable for the work.

Then F1 was injected into a semipreparative Buckyprep column with also chlorobenzene flow, collecting fraction 1-1 (F1-1) shown in figure 1b. The chemical species of this fraction assigned by LD-TOF-MS were $Ca@C_{94}$, $Ca@C_{90}$, $Ca@C_{96}$, $Ca@C_{92}$, C_{96}, C_{94}, C_{92} and so on. Further purification of F1-1 was performed with a semipreparative Buckyprep column (3ml/min flow rate; benzene eluent), collecting fraction1-1-1 (F1-1-1) within the period of 123 to 130min, and fraction1-1-2 (F1-1-2) 131 to 140 min (figure 1c). F1-1-1 mainly contained $Ca@C_{90}$ and $Ca@C_{92}$ confirmed by LD-TOF-MS, and were separated from each other completely using 5-PBB column with toluene flow (figure 1d). While $Yb@C_{90}(I)$, $Yb@C_{92}$ and $Yb@C_{90}$ (II) were separated from each other using Buckyprep-M column toluene as eluent recycled 3 rounds to more than 200 min.[6] Components in F1-1-2 measured by

LD-TOF-MS was $Ca@C_{94}$ and C_{94}, which had distinct retention time in Buckyprep-M column (figure 1e), and thus the purified $Ca@C_{94}$ was obtained. We selected 450 nm as detecting wavelength in the whole isolation process in order to avoid decomposing of the targets exposed in strong UV irradiation.

3. Results and discussion

Non-recycling four-step HPLC isolation of $Ca@C_{92}$ and $Ca@C_{94}$ with isomer free purities was accomplished by cooperation of three complementary HPLC columns joint with right mobile phase adopted. Absolute non-polarity of benzene solvent, and lower solubility of fullerenes and endohedral fullerenes in
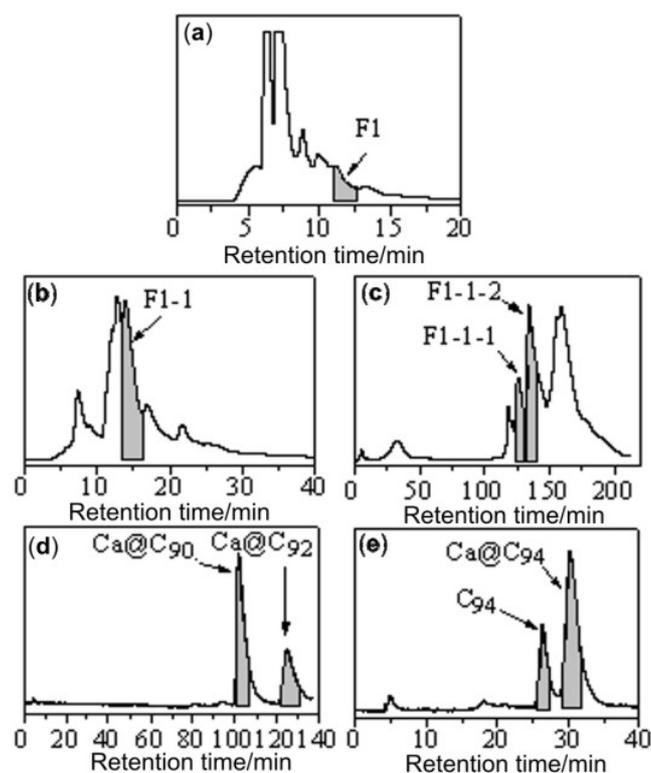
Figure 1. HPLC isolation schemes for $Ca@C_{92}$ and $Ca@C_{94}$. (**a**) The rough separation of raw extractant in chlorobenzene (Buckyprep-M $\phi 10 \times 250$ mm; 4 ml/min flow rate; chlorobenzene eluen). (**b**) Further purification of F1 (Buckyprep $\phi 10 \times 250$ mm; 4 ml/min flow rate; chlorobenzene eluent). (**c**) The third stage isolation (Buckyprep $\phi 10 \times 250$ mm; 3 ml/min flow rate; benzene eluent). (**d**) Complete separation of $Ca@C_{92}$ from $Ca@C_{90}$ (5-PBB $\phi 10 \times 250$ mm; 4·5 ml/min flow rate; toluene eluent). (**e**) Isolation of $Ca@C_{94}$ from F1-1-2 (Buckyprep-M $\phi 10 \times 250$ mm; 4·5 ml/min flow rate; toluene eluent).

benzene prolonged the retention time significantly, keeping both improved resolving level and perfect Gaussian absorption peak shapes at the same time. It is valuable for HPLC separations of fullerenes or endofullerenes without using expensive recycling devices or mixed flow such as addition of hexane into toluene. Figure 1c shown the important role of benzene flow very well, $Ca@C_{92}$ and $Ca@C_{94}$ eluted together retented for about 45 min utilizing toluene mobile phase instead on the same column with its compatible 4.5 ml/min flow rate.

The chemical purities of $Ca@C_{92}$ and $Ca@C_{94}$ was determined by LD-TOF-MS >98% shown in figure 2. Figure 3 shows their UV-Vis-NIR absorption spectra. $Ca@C_{92}$ has some characteristic peaks at 459, 633, 1188, and 1385 nm. It is similar to that of $Yb@C_{92}$.[6] We know that Ca possess constant +2 oxidation state in Ca-metallofullerenes, the similarity of UV-Vis-NIR absorption spectrum of $Yb@C_{92}$ and $Ca@C_{92}$ indicating that they may have similar molecular symmetries and Yb possess the same +2 oxidation state. But the UV-Vis-NIR absorption spectrum of $Dy_2@C_{92}$ (I, II, III)[4] and $Er_2@C_{92}$ (I, II, III, IV)[5] are quite different with $Ca@C_{92}$. We suggest that their molecular symmetries of C_{92} cage

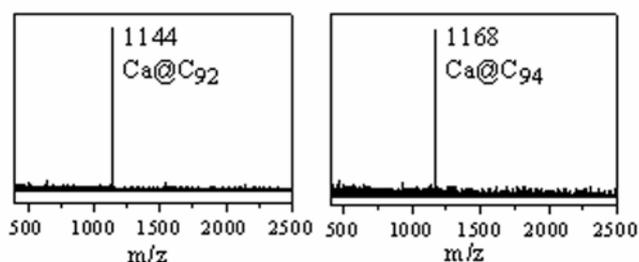are different from that of Ca. The UV-Vis-NIR absorption spectrum of $Ca@C_{94}$ shows large broad peaks at about 450–500, 600–700 and 750–900 nm. It is notable that $Ca@C_{94}$ and $Yb@C_{94}$ have almost the same absorption spectra.[6] Based on the above points, we suggest that Yb possesses +2 oxidation state in $Yb@C_{94}$. $Ca@C_{94}$ and $Yb@C_{94}$ have similar molecular symmetries too. There are still distinct differences between the absorption spectra of $Ca@C_{94}$ with that of $Dy_2@C_{94}$ (I, II)[4] and $Er_2@C_{94}$ (I, II).[5] Analogously we suggest $Dy_2@C_{94}$(I,II), $Er_2@C_{94}$ (I, II) have probably different molecular symmetries with that of $Ca@C_{94}$. The relative abundance of $Ca@C_{92}$ and $Ca@C_{94}$ is about 1 : 10. Moreover, when we separate F1-1 in Buckyprep column, we get a minor isomer of $Ca@C_{94}$ at about 140–150 min after the main peak F1-1-2 (figure 1c). This minor isomer has similar UV-Vis-NIR absorption spectrum with the major one, but the amount is too little to take further investigation, so this major $Ca@C_{94}$ may be the most stable or isolable one.

4. Conclusions

We have isolated and purified $Ca@C_{92}$ and $Ca@C_{94}$ effectively by using chlorobenzene as mobile phase. Calcium could be an indicator of charge state, since it has a constant +2 oxidation state in Ca-metallofullerenes that is different from rare earth metals. It is very helpful for us to estimate the oxidation state of rare earth metals in their endohedral metallofullerenes by comparing their UV-Vis-NIR absorption spectrum with that of Ca-metallofullerenes.

Figure 2. The LD-TOF-MS of $Ca@C_{92}$ and $Ca@C_{94}$.

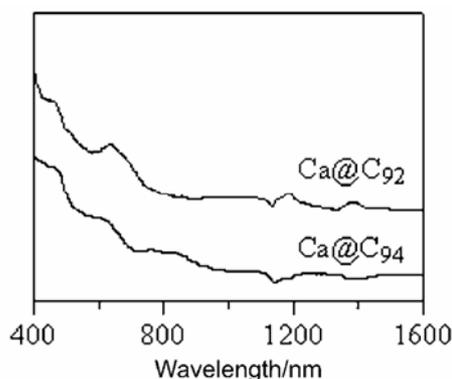**Figure 3.** The UV-Vis-NIR absorption spectra of $Ca@C_{92}$ and $Ca@C_{94}$ at room temperature in benzene solution.

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