Relative Yields of Endohedral Lanthanide Metallofullerenes by Arc Synthesis and Their Correlation with the Elution Behavior

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Fourteen endohedral lanthanide metallofullerenes were synthesized using the arc-discharge method under identical conditions, and their relative yields and elution behavior have been studied by mass spectrometry and HPLC. The eluate around the $M@C_{82}$ peak (M = lanthanide metal) was collected in two fractions of equal amount. The DCI negative ion mass spectrum of each metallofullerene in each collected fraction was well resolved on the basis of the characteristic isotopic distribution. The relative yield of these metallofullerenes was found to be in the following order: Ce > Pr > Tb > Gd > Nd > La ~ Er > Ho > Dy > Lu ≫ Tm ~ Sm ~ Eu ~ Yb. The order of their retention times (Tb > Gd > Pr > Ce > Er ~ Lu > La ~ Ho > Nd > Dy ≫ Tm ~ Sm ~ Eu ~ Yb) was also obtained by comparing the mass peak intensities of each metallofullerene from the two HPLC fractions. A fairly good correlation between these two sequences is identified and discussed.

Introduction

The successful extraction and isolation of macroscopic amount of endohedral metallofullerenes $M_n@C_{2m}$,[1–3] realized a few years ago, triggered a flood of research activities to produce and characterize these fascinating molecules. Most of the monometallofullerenes prepared so far have been based on C_{82} and group III metals (M= Sc, Y, La) and the majority of the lanthanide elements.[4–6] Due to difficulties in producing pure samples in large quantities, further experimental characterization of endohedral metallofullerenes has been hindered. To improve the production efficiency of metallofullerene, it is imperative to understand the mechanism of metallofullerene formation in the arc-discharge. To this end, we estimate that the relative yields of metallofullerenes and their relation to the elution behavior. We believe this is a first step toward this goal.

Despite many efforts, the relative yields of different metallofullerenes by arc discharge are still unknown quantitatively. Moro et al.[7] studied a variety of metallofullerene soots by laser and thermal desorption mass spectrometry. The metallofullerenes were classified into two groups on the basis of the intensity ratios ($M@C_{82}:M@C_{60}$) in the LD-MS spectra. According to the relative intensity ratios of $M@C_{82}$ to C_{60} in LD mass spectra, Sun et al.[8] also found that metallofullerenes of Ce, Pr, and Tb are most readily extracted by the "bomb" method and those of Sm, Eu, Tm, and Yb are more difficult to extract.

Recently, the chromatographic elution behavior of endohedral metallofullerenes has attracted some attention. Fuch et al.[9] studied the chromatographic retention of Ce-, Gd-, La-, and Y-containing endohedral metallofullerenes using [2-(1-pyrenyl)ethyl]silyl silica as stationary phase and toluene as eluent. The retention time sequence was found to be La@C_{82} < Ce@C_{82} < Gd@C_{82} < Y@C_{82}, which led to the inferences about the different degree of charge transfer and thus different effective dipole moments in these molecules. The unusual

upshift of the retention time Tm@C_{82} relative to that of La@C_{82} prompted Dunsch et al.[10] to assume the existence of divalent $Tm^{2+}@C_{82}{}^{2-}$, which was further proved by high energy spectroscopy.[11] HPLC elution behavior of many more lanthanide metallofullerenes were studied by Sueki et al.[12] using radio tracers, and some of them were identified by mass spectrometry.

All the experiments mentioned above involve separate preparation of individual metallofullerenes. The influences of such factors as the discharging conditions, extraction methods and characterization techniques, etc., on the relative yields may render the comparison unreliable. In the present study, we prepared all the 14 metallofullerenes under identical conditions, and their relative yields and chromatographic elution behavior were studied. The primary advantage of our approach is that the comparison is direct and thus the influences of preparative conditions on the metallofullerene yields can be avoided. The relative yields and chromatographic elution behavior of the metallofullerenes were obtained, and a fairly good correlation between them was discovered for the first time.

Experimental Section

The concurrent production of metallofullerenes containing different lanthanide metal atoms was carried out in a standard K–H type fullerene generator. Fourteen lanthanide oxides La_2O_3, CeO_2, Pr_6O_{11}, Nd_2O_3, Sm_2O_3, Eu_2O_3, Gd_2O_3, Tb_4O_7, Dy_2O_3, Ho_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, and Lu_2O_3 (with a purity of 99.95%, Shanghai Chemicals, Inc.) of equal metal mole fractions were put together, well ground, and then mixed uniformly with a graphite powder and a carbon cement (GC grade, Dylon, Inc.) to obtain a final atomic ratio of Ln:C = 0.02 (Ln = lanthanide elements). Graphite rods (i.d.: 6 × 100 mm) were drilled through (i.d.: 4.5 × 100 mm) and filled with the powder mixture of graphite and lanthanide oxides. The filled rods were baked under vacuum at 1100 °C for 3 h and subsequently used as the consuming anode for arc discharge. The "in situ activating"[13] and "back-burning"[14] techniques were

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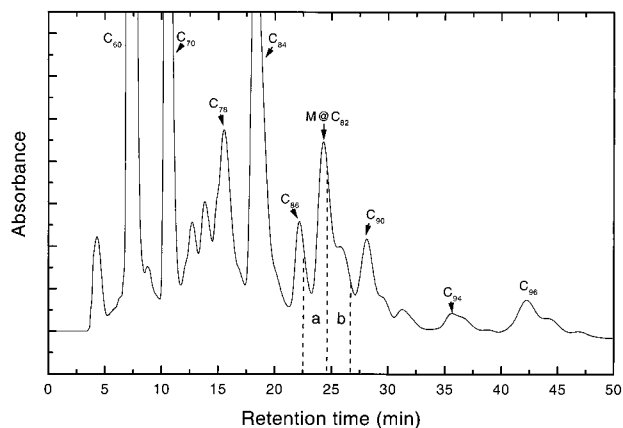

Figure 1. A typical HPLC profile of the redissolved DMF crude extract in toluene. The peak around 24.5 min was divided into two parts and collected separately as fractions a and b. The dividing line is set at an elution time of 24.5 min. Absorption at 330 nm was monitored for the HPLC analysis.

employed to increase the yields of lanthanide metallofullerene species. The arc-discharge conditions were as follows: electric current, 85 A; voltage, 25 ~ 30 V; He pressure, 125 Torr.

The carbon soot was collected and Soxhlet extracted with *N*,*N*-dimethylformamide (DMF, 99.9%, BDH) at its boiling temperature for 48 h to ensure the thoroughness of the extraction.[15] A dark brown solution was obtained after extraction. Removal of DMF by vacuum evaporation resulted in a black powder, which was then dissolved in toluene and filtered with a 0.2 μm disk filter (Rubbermaid, Inc.) before HPLC separation. Endohedral metallofullerene fractions were collected by HPLC using a PYE Cosmosil column (i.d.: 10 × 250 mm, Nacalai Tesque, Inc.) with toluene as the mobile phase. The injection volume was 5 mL and the elution rate was 4.0 mL/min. DCI negative ion mass spectrometry (Finnigan TSQ 7000) was used with methane for characterizing the composition of the samples.

Results and Discussion

A typical HPLC profile of the redissolved extract in toluene is shown in Figure 1. Aside from the off-scaled peaks of C_{60}, C_{70}, C_{84} and some peaks of other empty fullerenes, a sizable peak appears at an elution time of ~24.5 min. This peak is absent for the samples produced from arc discharge of a pure carbon electrode, and apparently, it corresponds to the mixture of $Ln@C_{82}$. This was verified by mass spectrometry which will be described below. As indicated in Figure 1, this peak was divided into two parts and collected separately as fractions a and b. The dividing line is set at an elution time of 24.5 min.

Figure 2a and b show the DCI negative ion mass spectra of the lanthanide metallofullerenes in fraction a and fraction b, respectively. In the mass range from $m/z = 1123$ to $m/z = 1165$, the isotopic distribution of lanthanide metallofullerenes $Ln@C_{82}$ can be clearly observed. Considering that the individual mass peak intensities depend on the sampling time of the DCI mass spectrometer (see the insets), we integrated the signals over the whole envelope of metallofullerene evaporation. Figure 2a and b were recorded at the maxima of the metallofullerene evaporation profiles, which are quite similar to the mass spectra integrated over the evaporation profiles (see Figure 3a and b).

Figure 3a and b are the DCI mass spectra of the HPLC fractions a and b integrated over the metallofullerene evaporation profiles. Due to the broad range of lanthanide metal isotopes,
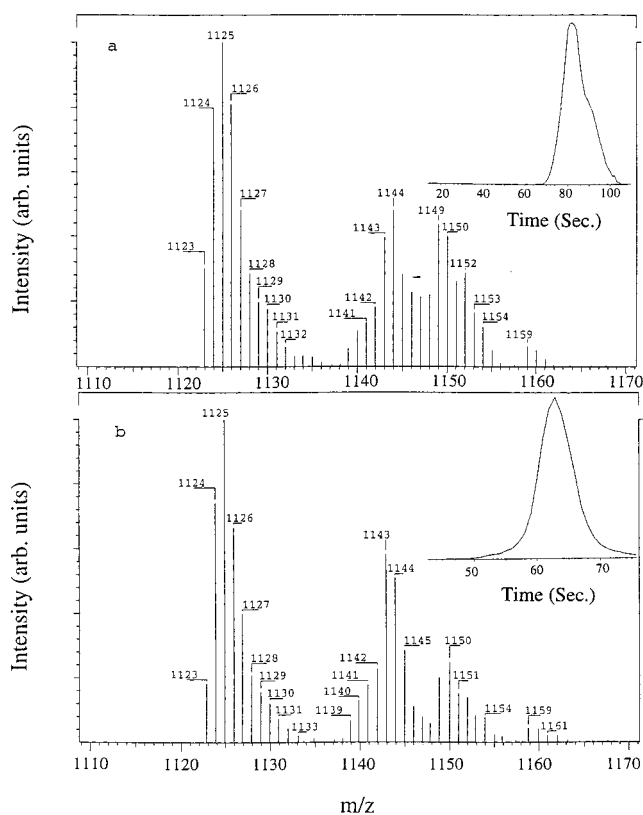

Figure 2. Methane DCI negative ion mass spectra of the lanthanide metallofullerenes from HPLC fraction a and fraction b (see Figure 1), respectively. The insets show the intensities of the metallofullerenes as a function of the evaporation sampling time of the DCI mass spectrometer.

the mass spectra show significant overlap among the peaks of different metallofullerenes. Fortunately, the contribution of each metallofullerene to the mass spectra can be recognized through its characteristic natural isotope distribution as shown in the spectra. In fitting the mass spectra, we made use of a few m/z peaks for which over 99% can be contributed to an individual metallofullerene (e.g., $m/z = 1123$: 99.6% from $La@C_{82}$; $m/z = 1140$, 99.5% from $Gd@C_{82}$). The overall contour in the mass spectra can be well reproduced by fitting the contributions from different metallofullerenes with a characteristic isotope distribution. The error from such data treatments is less than 5% as estimated from our separate experiments and data analysis.

Figure 4 gives graphically the relative abundance of each metallofullerene deconvoluted from the isotope distributions in Figure 3. Further summation over the relative abundance in HPLC fraction a (curve a) and fraction b (curve b) gives the total relative yield of each metallofullerene (curve c). The order of the relative yields is found to be: Ce > Pr > Tb > Gd > Nd > La ~ Er > Ho > Dy > Lu ≫ Tm ~ Sm ~ Eu ~ Yb. Of all the metallofullerenes we produced, $Ce@C_{82}$, $Pr@C_{82}$, and $Tb@C_{82}$ are the highest in relative yields, $Tm@C_{82}$, $Sm@C_{82}$, $Eu@C_{82}$, and $Yb@C_{82}$ are the lowest. This is in general consistent with the results of Moro et al.[7] and Sun et al.[8] with some variation. More data are detailed in Table 1, which lists some physical properties of lanthanide elements, relative yields, relative retention times of $M@C_{82}$, and a few reference data.

The relative retention time of each metallofullerene can be related to the relative amount of this metallofullerene in the fractions a and b. The more of this metallofullerene in the fraction b, the longer its retention time will be. If a triangular elution peak is assumed, the retention time is proportional to

TABLE 1: Physical Properties of Lanthanide Elements, Relative Yields (M@C$_{82}$:La@C$_{82}$), Relative Retention Times (M@C$_{82}$:La@C$_{82}$) and Some Reference Data^a

| element | electronic configuration | oxide state | ionic radii (pm) | inization energies | | relative yield (M@C$_{82}$: La@C$_{82}$) | relative yield | | relative retention time (M@C$_{82}$: La@C$_{82}$) | retention time (min) |
				I_3	$I_{4(kJ/mol)}$		ref 7	ref 8		
La	5d6s^2	+3	106.1	1850	4819	1	1	1	1	
Ce	4f^{1}5d^{1}6s^2	+3, +4	103.4, 92	1949	3547	2.32	0.31	2.02	1.10	24.33
Pr	4f^{3}6s^2	+3, +4	101.3, 90	2086	3761	1.69	0.31	2.50	1.12	24.52
Nd	4f^{4}6s^2	+3	99.5	2130	3899	1.41	0.46	0.72	0.94	
Sm	4f^{6}6s^2	+2, +3	111, 96.4	2260	3990	0.02	0.07	0.07		
Eu	4f^{7}6s^2	+2, +3	109, 95	2404	4110	0	<0.07	0.02		
Gd	4f^{7}5d^{1}6s^2	+3	93.8	1990	4250	1.50	1.1	0.61	1.16	25.01
Tb	4f^{9}6s^2	+3, +4	92.3, 84	2114	3839	1.59	0.31	2.05	1.21	
Dy	4f^{10}6s^2	+3	90.8	2200	4501	0.83		0.50	0.71	
Ho	4f^{11}6s^2	+3	89.4	2204	4150	0.88	0.31	0.45	0.98	23.60
Er	4f^{12}6s^2	+3	88.1	2194	4115	0.97	0.62	0.40	1.05	
Tm	4f^{13}6s^2	+2, +3	94, 86.9	2285	4119	0.07		0.21		
Yb	4f^{14}6s^2	+2, +3	93, 85.8	2415	4220	0.006	<0.07	0.05		
Lu	4f^{14}5d^{1}6s^2	+3	85	2022	4360	0.22	0.69		1.06	24.05

^{a} The data from ref 7 (M@C$_{82}$:M@C$_{60}$) and ref 8 (M@C$_{82}$:C$_{60}$) were normalized to those of La@C$_{82}$ for easy comparison to our data. Since the data from refs 7 and 8 were obtained from unseparated samples, the contribution from empty fullerenes C$_{94}$ ($m/z = 1128$), and C$_{96}$ ($m/z = 1152$) might influence the results of Nd@C$_{82}$ ($m/z = 1128$), Er@C$_{82}$ ($m/z = 1151$), and Tm@C$_{82}$ ($m/z = 1153$).
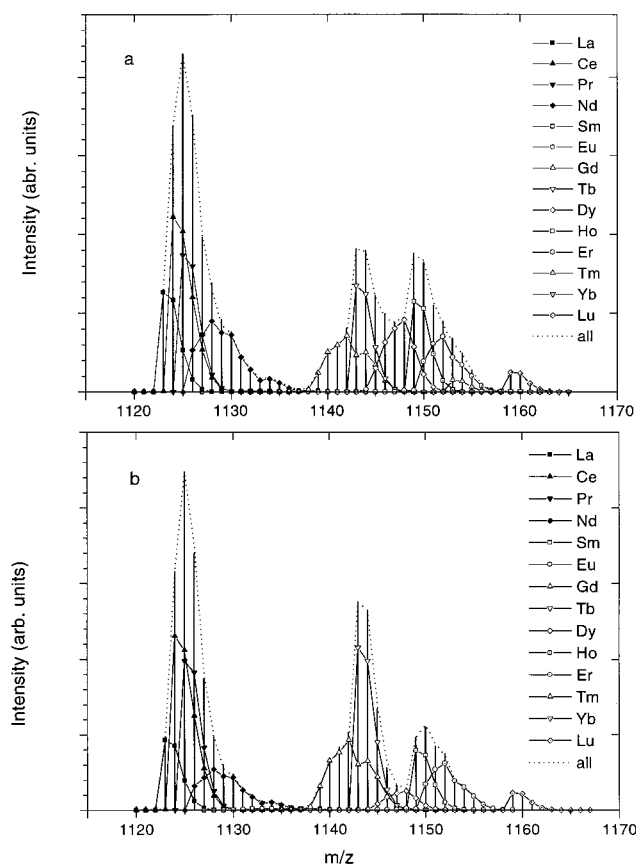

Figure 3. Methane DCI negative ion mass spectra of the HPLC fractions a and b integrated over the corresponding metallofullerene evaporation profiles for each metallofullerene. The overall envelope (dotted lines) in the mass spectra can be well reproduced by fitting the contributions from different metallofullerenes with a characteristic isotope distribution.

Figure 4. The relative abundance of each metallofullerene deconvoluted from the isotope distributions in Figure 3. Further summation over the relative abundance in fraction a (curve a) and fraction b (curve b) gives the total relative yield of each metallofullerene (curve c).

for metallofullerenes containing the first four lanthanide elements (La, Ce, Pr, Nd), both curves follow Ce > La and Pr > Nd. Third, for the middle five elements (Gd to Er), the order is exactly the same for both curves: Tb > Gd > Er > Ho > Dy. Some minor differences between the two curves are also noticeable. For example, for the light rare earth elements (La, Ce, Pr, Nd), the relative yields of metallofullerene production are Ce > Pr, Nd > La, but this order is reversed in relative retention times. In addition, in the relative retention time curve, the data points representing heavy rare earth elements (Gd, Tb, Ho, Er, and Lu) containing metallofullerenes shift upward in comparison to those in the relative yield curve c in Figure 4. It should be pointed out that the results we obtained for La@C$_{82}$, Ce@C$_{82}$, and Gd@C$_{82}$ are consistent with the published results in retention time.[9] In addition, we verified the above retention time sequence in separate preparations of the 14 lanthanide metallofullerenes by using one metal at a time. The results of HPLC measurements are given in Table 1.

For convenience of direct comparison, we normalized both the relative yields and retention times to those of La@C$_{82}$; the results are shown as curve 1 and curve 2 in Figure 6, respectively. The normalized relative retention times of Sm-, Eu-, Tm- and Yb-containing metallofullerenes were not obtained in this study since their signals were completely absent in the HPLC fraction b. We therefore simply took their normalized relative retention times as zero.

the square root of the relative amount of the metallofullerene in fraction b, i.e., $[b/(a + b)]^{1/2}$, where a and b represent the intensities of curves a and b in Figure 4, respectively.

Shown in Figure 5 is the plot of relative retention times ($[b/(a + b)]^{1/2}$) as a function of encaged metal identities. Compared with curve c in Figure 4, the curve in Figure 5 is surprisingly similar in shape. First of all, Sm-, Eu-, Tm-, and Yb-containing metallofullerenes are in the valley for both curves. Second,
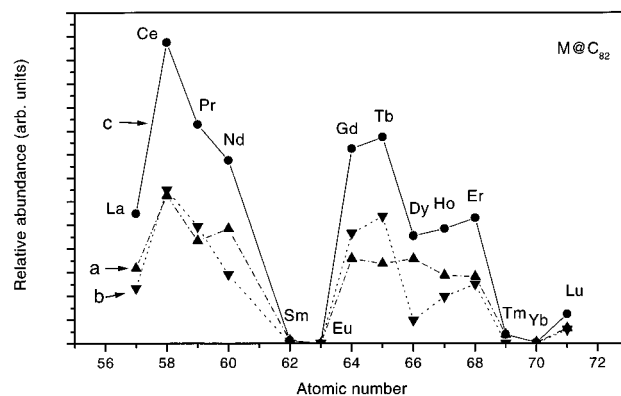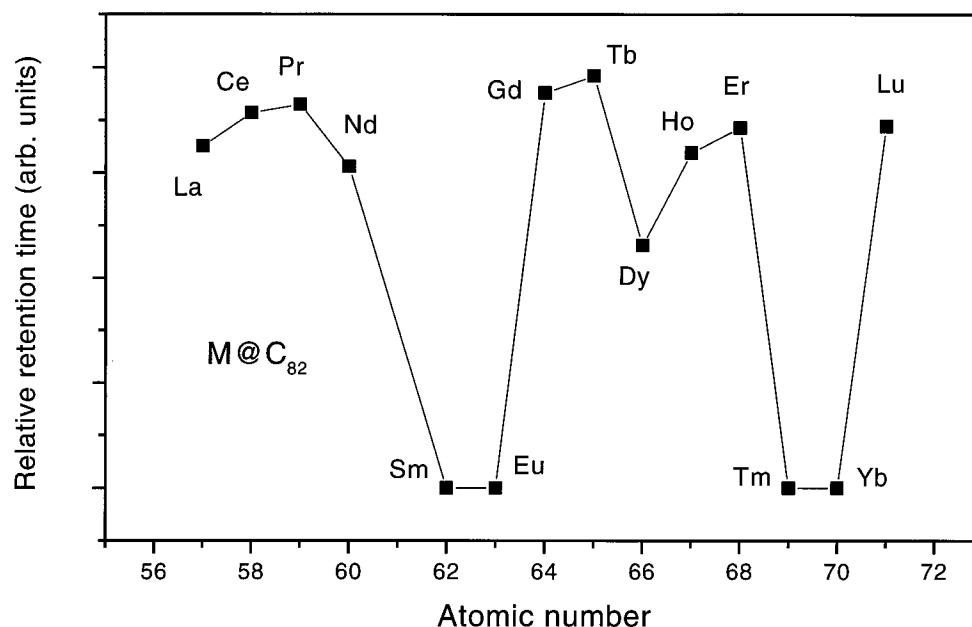
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Figure 5. The plot of relative retention times as a function of encaged metal identities. The relative retention times are obtained by taking the square root of the relative amount of the metallofullerenes in faction b.
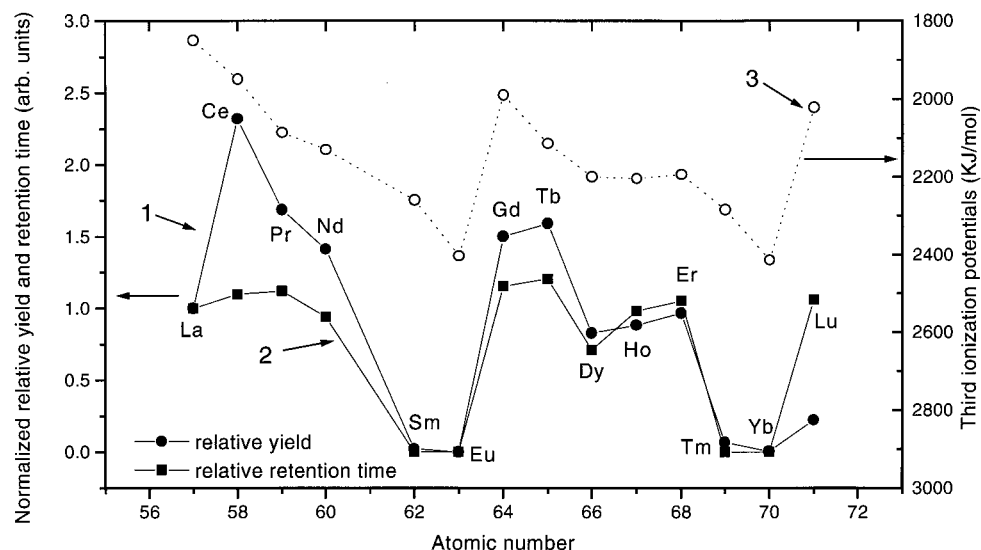

Figure 6. Normalized relative yields (curve 1) and relative retention times (curve 2). Curve 3 shows the third ionization potentials of lanthanide elements.

The general trend in Figure 6 is noteworthy. It shows that the higher the relative yield, the longer the relative retention time. According to the study on the chromatographic elution behavior of metallofullerenes (Y, La, Ce, Gd),[9] the difference in retention time is related to the charge transfer in these molecules and the resulting effective dipole moments. This then suggests that the metallofullerenes with higher relative yields may also have a higher degree of charge transfer or a higher effective dipole moment. This can be understood if the formation of metallofullerene in the arc plasma involves the formation of metal−carbon clusters as metallofullerene precursors.[14,16] The greater extent of the charge transfer, the more easily the metal−carbon clusters form at high temperature, and consequently the higher the relative yield of the metallofullerene. The exceptionally high yields of Ce@C_{82} and Tb@C_{82} in comparison with those of other metallofullerenes might be attributed to the facile formation of $(CeC_2)_n$ and $(TbC_2)_n$ at high temperature. In fact, CeC_2 nanocrystals encapsulated in graphite

cages were identified by TEM and other techniques.[17,18] If these metal carbon clusters are precursors of metallofullerenes, Ce@C_{82} yield would be greatly enhanced. Since the valence state of Ce^{3+} has been suggested by the XPS study,[5] the final step of metallofullerene formation from the metal−carbon clusters may embrace the transformation process of Ce^{4+} → Ce^{3+}.

To make further progress, The third ionization potentials of lanthanide elements (Ln[2+] → Ln[3+]) are also presented in Figure 6 (curve 3).[19] It is remarkable that the overall shape of this curve is quite similar to those of curves 1 and 2. This constitutes another evidence that for metallofullerenes of the type M@C_{82}, the trivalent form is preferred to the divalent and thus lead to higher yields. In fact, the trivalent nature of a host of metallofullerene have been confirmed. Furthermore, as mentioned above, the high valent metal−carbon clusters are more stable. A high metallofullerene yield is expected if these species are precursors.

Conclusion

In conclusion, we have obtained, for the metallofullerenes $M@C_{82}$, the first systematic and quantitative experimental values of the relative yields and relative retention times in a 5PYE column using toluene as eluent. The approximate linear relationship between the relative yields and relative retention times and other properties of lanthanide elements was revealed. The general trends of these two curves were explained and may be helpful for elucidating the formation mechanism of endohedral metallofullerenes, thereby increasing the efficiency of preparation and facilitating further characterization of metallofullerenes for new properties.

References and Notes

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