Different Extraction Behaviors between Divalent and Trivalent Endohedral Metallofullerenes

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On the basis of high-yield preparation, arc-produced soot containing endohedral Y, La, Nd, Sm, Gd, Tb, Yb, Ca, and Ba fullerenes are successively extracted with carbon disulfide, *N*,*N*-dimethylformamide, pyridine, and aniline. The continuous four-step extraction procedure generates endohedral metallofullerenes (EMFs) with high content and abundant species, and novel EMFs such as Tb@C_{66}, Yb@C_{60}, and Tb_3@C_{80} were extracted. This makes it possible for us to systemically study the varying extraction behaviors of divalent and trivalent metallofullerenes. Trivalent EMFs are characterized by higher content and multimetallofullerenes, whereas divalent species are characterized by lower content and solely monometallofullerenes. A positive relationship between the content and the species abundance of EMFs is proposed. The differences in extracting ability of the above solvents toward certain EMFs are summarized and explained on the basis of the number of transferred electrons from the encaged metal atom(s), the back-donation from carbon cages, and the solvent reduction of EMFs.

1. Introduction

Since the first extraction of endohedral metallofullerenes (EMFs),[1] an intense effort has been made on the preparation, isolation, and characterization of these novel species. To obtain macroscopic amounts of EMFs pure enough for chemical and physical characterization, solvent extraction followed by high-performance liquid chromatography (HPLC) isolation is exclusively applied to the raw soot generated by dc arc discharge or laser ablation technique.[2,3] Because of low-yield preparation and limited solubility in common organic solvents, only those EMFs mainly based on the C_{82} cage have been isolated in milligram quantities.[4] It is expected that EMFs will show varying special properties depending upon the fullerene size and the kind and the number of encapsulated metal atoms. Therefore, it is very important to attain a large amount of EMFs with plentiful species for their scientific research and technical development.

Apart from efforts on optimization of preparation conditions,[5−9] researchers paid much attention to the solvent extraction of EMFs from raw soot. To date, three methods, that is, Soxhlet extraction, high-temperature high-pressure "bomb" extraction,[10,11] and low-temperature supersonic extraction,[12] have been developed. The solvents used are limited to toluene, 1,2,4-trichlorobenzene (TCB), xylene, carbon disulfide, pyridine, *N*,*N*-dimethylformamide (DMF), and aniline. Carbon disulfide is found a good solvent both for EMFs and for empty fullerenes. Pyridine and DMF are reported to be of selective extracting ability toward M@C_{82}, M@C_{80}, and M_2@C_{80}[11,13,14] and aniline toward M@C_{60} and M@C_{70}.[12] In practice, two-step extraction was usually employed to enrich EMFs.[15−17] A large amount of C_{60}, C_{70}, and other empty fullerenes are first extracted with toluene, xylene, or carbon disulfide, and the residues are further extracted with carbon disulfide, DMF, or pyridine, and then a concentrated extract is available for further HPLC isolation.

The HPLC elution behaviors of 14 endohedral lanthanide metallofullerenes were investigated previously.

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Table 1. Solvent Extraction Yields of Various Soot Samples Containing EMFs

	yield of the extract of EMF containing soot, %[a]						
solvent	Tb	Y	La	Gd	Sm	Yb	Ca
CS_2	3.0	2.8	2.7	2.7	2.4	1.9	2.2
DMF	7.2	6.8	6.3	5.8	2.1	1.8	1.8
pyridine	1.5	1.4	1.4	1.2	0.3	0.2	0.2
aniline	1.2	1.2	1.1	1.0	0.18	0.15	0.16

[a] Yield $= W_e/W_s \times 100\%$; W_e = weight of solvent extract; W_s = weight of carbon in soot.

Sueki et al.[18] divided the lanthanide EMFs into divalent and trivalent groups in line with the difference in retention time. Huang and Yang[19] proposed an approximate linear relationship between the relative yield and relative retention time. However, it should be mentioned that only TCB or DMF was used to extract lanthanide EMFs in the above works, and some extractable species still exist in the residues. Because of low-yielded preparation and inefficient extraction, systematic studies on the HPLC elution behaviors are exclusively limited to C_{82}-based monometallofullerenes.

Recently, we reported high-yielded preparation of EMFs by an improved dc arc discharge method.[5,20] In the present work a successive four-step solvent extraction procedure was applied to the soot containing divalent and trivalent EMFs. Mass spectrometric studies show that not only the contents but also the numbers of EMFs species increase. This makes it possible to systematically investigate the extraction behaviors of EMFs with varying organic solvents.

2. Experimental Section

Soot containing EMFs was produced by an improved dc arc discharge method.[5,20] The anode is a $\phi 6 \times 150$ mm specpure graphite rod drilled with a $\phi 4.5 \times 120$ mm hole and filled with a powder mixture of graphite and M-Ni alloy (MNi_2) (M = Y, La, Nd, Sm, Gd, Tb or Yb) in an atomic ratio of M/C = 0.1. In the case of endohedral Ca and Ba fullerenes preparation, CaC_2 grains and Ba flakes were used as the encaged metal source, respectively. The cathode is a ϕ10-mm specpure graphite rod with a tapered end pointing to the anode to lessen the formation of cathode deposit. An arc was generated at 50A in a helium static atmosphere of 720 Torr, keeping the distance between anode and cathode about 12 mm by adjusting the anode forward.

For the preparation of a specific species of EMFs, four doped rods were burned and 15−20 g of soot was produced. The soot collected was first subjected to Soxhlet extraction with carbon disulfide for 24 h. A Ti tube with 4-μm pores on the wall was used to hold carbon soot to not leak much fine carbon soot out. The residues after drying in a vacuum at 80 °C for 12 h were further Soxhlet-extracted by DMF and pyridine successively until the color of the fresh extract was undiscernible. Finally, the residues were dispersed supersonically in aniline for 2 h at room temperature, and the resulting sludge was filtered with a 2−3-μm glass grit filter. To get rid of coexisting fine soot completely, the DMF, pyridine, and aniline extracts were centrifuged at 24 000 rpm for 30 min, respectively. Such obtained solutions were evaporated, and the residues were dried for 8 h at 100 °C in a vacuum and weighed. Table 1 shows the experimental data related to the yields of different extracts of various soot samples containing EMFs. It should be mentioned that the data shown here reflect the weight ratios of all the solvent soluble substances to carbon in soot. Normally, the content of EMFs in raw soot is less than 1.5%.[4]

All of the above extracts and raw soot were analyzed by laser desorption mass spectrometry (MALDI-TOF, BIFLEX III, Bruker Inc.). A small piece of raw soot and a proper amount of toluene were put into an alumina mortar and ground into a stable suspension. The samples were coated on a stainless steel plate by drying the toluene suspensions or different solvent extracts at ambient temperatures or by gently heating to <100 °C. Radiation pulses (10^{-8} s) from a N_2 laser operating at 337 nm were used to desorb the specimens from the plate, and the positive ions formed were detected in a reflection mode.

3. Results

3.1. EMFs in Raw Soot. To estimate the relative abundance of varying EMFs and the effectiveness of successive solvent extraction, the arc-produced soot was first analyzed. Figure 1 shows the MALDI-TOF mass-spectra of the raw soot containing (a) Yb, (b) Gd, and (c) Tb EMFs, among which Figures 1a and 1b are typical mass spectra of divalent and trivalent metallofullerenes, respectively.

Observed in Figure 1a are a series of weak broad peaks, which can be assigned to the combined peaks of monometallofullerenes $Yb@C_{2n}$ ($2n \geq 60$) and empty fullerenes C_{2n+14}. It is obvious that the peak intensities of Yb EMFs are much lower than that of C_{60} and C_{70}, and no multimetallofullerenes are detected. In Figure 1b two sets of broad peaks owing to the large distribution of five isotopes of Gd (155: 14.8%, 156: 20.5%, 157: 15.7%, 158: 24.8%, 160: 21.9%)[21] are observed. One set is ascribed to monometallofullerenes $Gd@C_{2n}$ ($2n = 54-136$), and the other is assignable to the combined peaks of dimetallofullerenes $Gd_2@C_{2n}$ ($2n = 58-124$) and empty fullerenes C_{2n+26}, which is a result of the coincidence in mass numbers between gadolinium and carbon. Of interest to note is that all of the strong peaks are from Gd EMFs except those from C_{60} and C_{70}, and the peak intensity of $Gd@C_{82}$ is comparable to that of C_{70}. As shown in Figure 1c, nearly all of the discernible peaks are assignable to monometallofullerenes $Tb@C_{2n}$($2n \geq 58$) and dimetallofullerenes $Tb_2@C_{2n}$ ($2n \geq 56$). It should be noted that the peaks of C_{60} and C_{70} are extremely low in intensity, and those from other empty fullerenes are too weak to be detected, which is indicative of much higher abundance of Tb EMFs than that of Yb and Gd species in the soot.

The soot containing other divalent or trivalent EMFs studied in this work shows similar mass spectroscopic results to that of Yb or Gd EMFs (see Figure S1). The similarities are clearly shown in Table 2, which lists the peak intensity ratios of $M@C_{2n}$:C_{60} and $M@C_{2n}$:$M@C_{60}$. From Table 2 it can be seen that the peak intensity ratios of $M@C_{2n}$:C_{60} for the trivalent EMFs are approximately 10 times those of divalent ones, implying higher abundance of trivalent EMFs than divalent species in the soot. Moreover, apart from monometallofullerenes, dimetallofullerenes are commonly observed in the mass spectra of the soot containing trivalent EMFs. In contrast, only monometallofullerenes are observed for divalent species. Therefore, the mass spectra of the raw soot reveal two groups of EMFs on the basis of the peak intensity ratios $M@C_{2n}$:C_{60} and the

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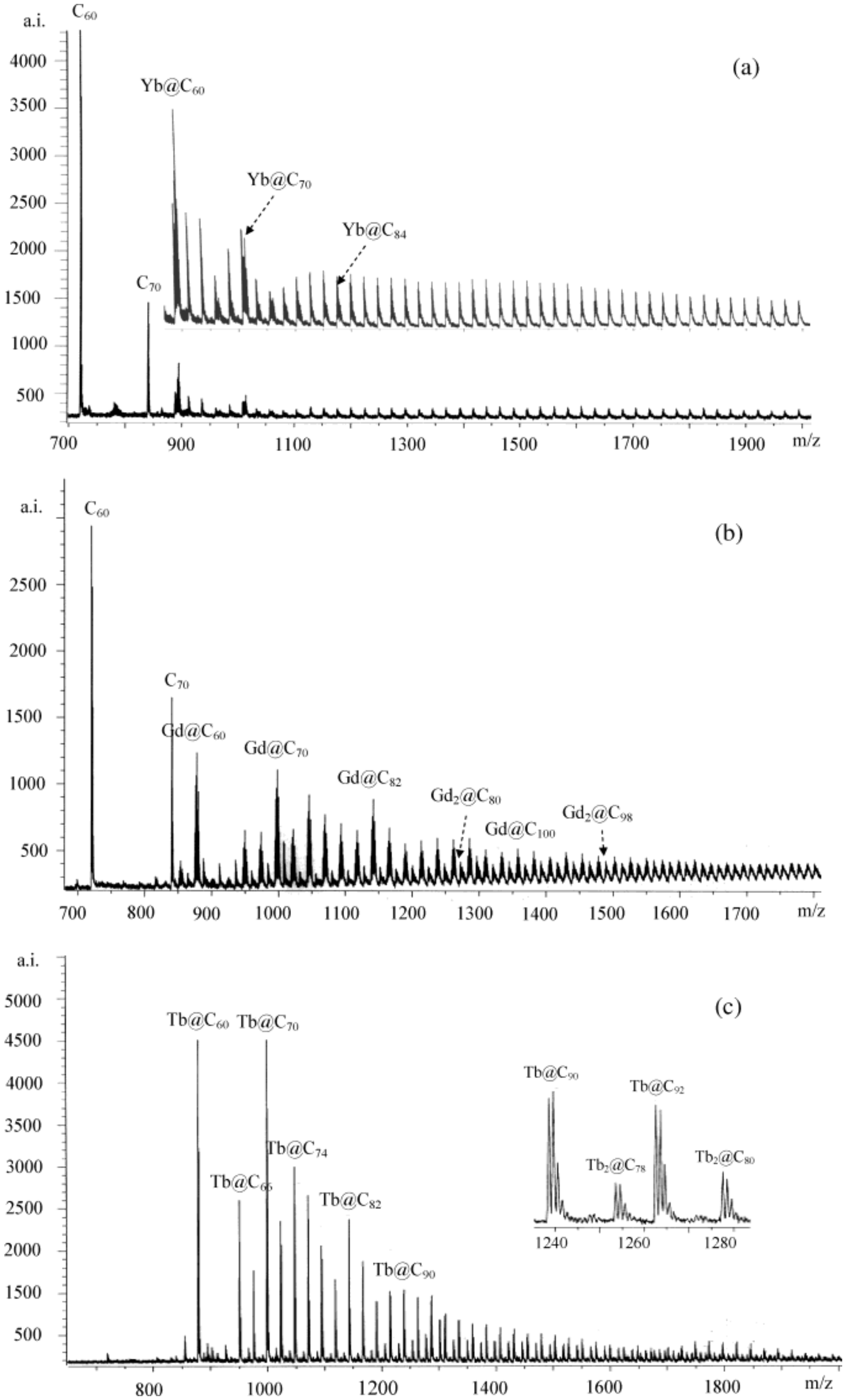

Figure 1. MALDI-TOF mass spectra of the raw soot containing (a) Yb, (b) Gd, and (c) Tb EMFs.

multiplicity in EMF species, which could be correlated with the oxidation state of encaged metal atoms.

Moro et al.[22] investigated a variety of alkaline earth and rare earth EMFs in the arc-produced raw soot. On the basis of the metallofullerene ratios M@C_{2n}:M@C_{60} found in the laser desorption mass spectra, EMFs were classified into two groups. The trivalent group comprises Sc, Y, La, Ce, Pr, Nd, Gd, Tb, Ho, Er, and Lu EMFs, whereas the divalent group includes those of Ca, Sr, Sm, Eu, and Yb. It is obvious that our grouping result is consistent with theirs. However, we should note that the base for classification is quite different. They separate EMFs into divalent and trivalent groups in accordance with the ratios of M@C_{70}, M@C_{74}, and M@C_{82} to M@C_{60}. In the case of the trivalent group, the ratio of M@C_{74} or M@C_{82} to M@C_{60} is equal to or larger than the ratio of M@C_{70} to M@C_{60}, whereas the ratios for M@C_{74} and M@C_{82} in the divalent group are all less than that for M@C_{70}. As Table 2 shows, this grouping criterion does not fit to our mass spectral data since M@C_{60} and M@C_{70} are always observed to be of the strongest intensities in our mass spectra, regardless of the oxidation states of the encaged metal atom(s).

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Table 2. Peak Intensity Ratios $M@C_{2n}$:C_{60} and $M@C_{2n}$:$M@C_{60}$ (in Parentheses)

element	$M@C_{60}$	$M@C_{66}$	$M@C_{70}$	$M@C_{74}$	$M@C_{82}$	$M@C_{84}$
			Trivalent Group			
Y	0.9(1)	0.54(0.6)	0.63(0.7)	0.45(0.5)	0.27(0.3)	0.18(0.2)
La	0.8(1) *0.019*[a]	0.2(0.3)	0.6(0.8) *0.012(0.6)*	0.4(0.5) *0.025(1.3)*	0.4(0.5) *0.025(1.3)*	0.3(0.4
Gd	0.4(1) *0.05*	0.2(0.6)	0.3(0.9) *0.023(0.5)*	0.3(0.8) *0.05(1.0)*	0.2(0.7) *0.07(1.4)*	0.2(0.4)
Tb	46(1)	23(0.5)	46(1)	26(0.6)	21(0.5)	19(0.4)
			Divalent Group			
Sm	0.1(1)	0.05(0.3)	0.1(0.6)	0.05(0.4)	0.043(0.3)	0.05(0.4)
Yb	0.1(1)	0.01(0.1)	0.04(0.3)	0.01(0.1)	0.006(0.05)	0.01(0.1)

[a] Italic data from ref 22.

Furthermore, we found that the peak intensity of all the EMFs in the trivalent group is much stronger than that of their neighboring empty fullerenes in the region of $m/z = 850-1600$. In contrast, the EMFs observed by Moro and co-worker are much weaker than their neighboring empty fullerenes, and very few dimetallofullerenes are detected in the mass spectra. Considering the data listed in Table 2, we could conclude that the abundance of EMFs in the raw soot increases tens of times with our improved procedure.

3.2. EMFs in Carbon Disulfide Extracts. Shown in Figure 2 are the MALDI-TOF mass spectra of carbon disulfide extracts containing Yb, Ca, Gd, and Tb EMFs. From Figure 2a it can be seen that the extraction behaviors of Yb EMFs are quite similar to that of Sm species.[5] Apart from the very strong peaks owing to empty fullerenes, such as C_{60}, C_{70}, C_{76}, C_{78}, C_{82}, and C_{84}, we observed a series of weak peaks originating from monometallofullerenes $Yb@C_{2n}$ ($2n = 72-100$) with $Yb@C_{84}$ and $Yb@C_{90}$ as the most abundant species. As in the case of raw soot, no multimetallofullerenes are detected.

Similarly, a series of monometallofullerenes, $Ca@C_{2n}$ ($2n = 72-136$), with $Ca@C_{84}$ and $Ca@C_{90}$ as the most abundant species are observed in Figure 2b. However, comparing with other divalent species such as Ba EMFs (see Figure S2), Ca metallofullerenes show some different extraction behaviors in higher abundance and more species of monometallofullerenes and a series of weak dimetallofullerenes $Ca_2@C_{2n}$ ($2n = 88-128$). The larger diameter of Ba^{2+} cation compared to that of Ca^{2+} cation is thought to be a factor responsible for their difference in preparation yield.[23] However, we should keep in mind that Ca and Ba EMFs were prepared with CaC_2 grains and Ba flakes as the encaged metal source, respectively. The dissociation temperature of CaC_2 is much higher than the boiling point of metal Ba. Thus, Ca atoms have a greater chance to coevaporate with graphite carbon to form EMFs than Ba atoms. We argue that this is the real reason leading to the difference in extraction behavior between Ca and Ba EMFs. In fact, high-yield Ba monometallofullerenes $Ba@C_{2n}$ ($2n = 74-136$) along with a series of minor dimetallofullerenes, $Ba_2@C_{2n}$ ($2n = 88-116$), were produced by coevaporating graphite and metal barium.[9] Here is shown the important effect of doping materials on the preparation of EMFs.

From Figure 2c, we find a series of Gd monometallofullerenes, $Gd@C_{2n}$ ($2n = 72-114$), and dimetallofullerenes, $Gd_2@C_{2n}$ ($2n = 78-138$). Though $Gd_2@C_{78}$ and $Gd_2@C_{80}$ were reported being extracted from their raw soot with pyridine and DMF,[11,14] it is novel for us to extract a series of Gd dimetallofullerenes with carbon disulfide. The peak intensity for monometallofullerenes decreases in the following order $Gd@C_{82} > Gd@C_{76} > Gd@C_{94} > Gd@C_{90}$, and a hunchbacked distribution in the peak intensity of Gd dimetallofullerenes is observed around the m/z of $Gd_2@C_{100}$. In the MALDI-TOF mass spectrum of carbon disulfide extract containing Y EMFs (see Figure S2), a series of peaks from monometallofullerenes, $Y@C_{2n}$ ($2n = 72-106$), and dimetallofullerenes, $Y_2@C_{2n}$ ($2n = 72-122$), are identified. The monometallofullerenes follow an order in peak intensities of $Y@C_{82} > Y@C_{76} > Y@C_{94} > Y@C_{90}$, similar to that of Gd monometallofullerenes. A hunchbacked distribution in the peak intensity of Y dimetallofullerenes is also found around the m/z of $Y_2@C_{92}$ besides a special high intensity of $Y_2@C_{82}$.

Among the EMFs studied in this work, Tb EMFs are of the highest abundance and of the most plentiful species, that is, with the biggest number of metal atoms encapsulated in a wide range of fullerene cages. Three categories of Tb EMFs are observed in Figure 2d: monometallofullerenes $Tb@C_{2n}$ ($2n = 66,72-106$) with intensity following the order $Tb@C_{82} > Tb@C_{76} > Tb@C_{94} > Tb@C_{90} > Tb@C_{84}$; dimetallofullerenes $Tb_2@C_{2n}$ ($2n = 72-140$) with intensities decreasing monotonically outward from the central m/z of $Tb_2@C_{102}$; and trimetallofullerenes $Tb_3@C_{2n}$ ($2n = 80, 92-120$) with $Tb_3@C_{80}$ as the most abundant species. It is novel for us to synthesize and extract a series of Tb trimetallofullerenes. Given that the peaks from Tb trimetallofullerenes are too weak to be detected in the mass spectrum of the raw soot, we argue that carbon disulfide has special extraction selectivity toward these new species. Moreover, all of the strong peaks belong to Tb EMFs and those owing to empty fullerenes including C_{60} and C_{70} are very weak, suggesting higher content of Tb EMFs in the extract than the other metal species and strong extracting ability of carbon disulfide toward them.

Detailed analysis of the carbon disulfide extracts of a large variety of alkaline earth and rare earth EMFs leads to a positive correlation between the content and the species abundance of EMFs. In Figure 2 we observed more species of Ca EMFs than Yb ones, including monometallofullerenes $Ca@C_{2n}$ ($2n > 100$) and a series of dimetallofullerenes. On the other hand, Ca EMFs show the largest peak intensity ratios $M@C_{2n}$:C_{60} among the divalent EMFs studied in this work. Deduced from the peak intensity ratios $M@C_{84}$:C_{60} in the mass spectra,

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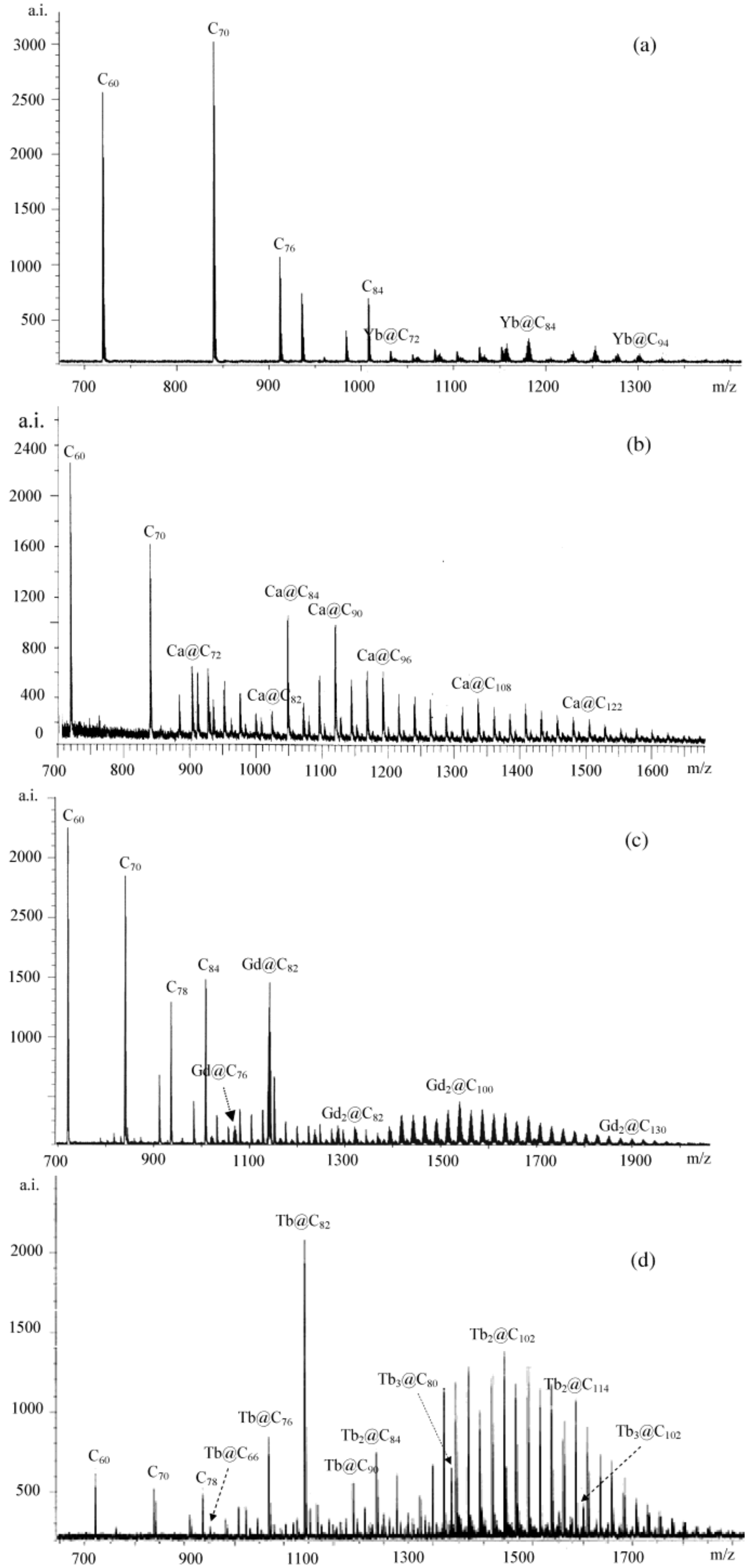

Figure 2. MALDI-TOF mass spectra of the carbon disulfide extracts containing (a) Yb, (b) Ca, (c) Gd, and (d) Tb EMFs.

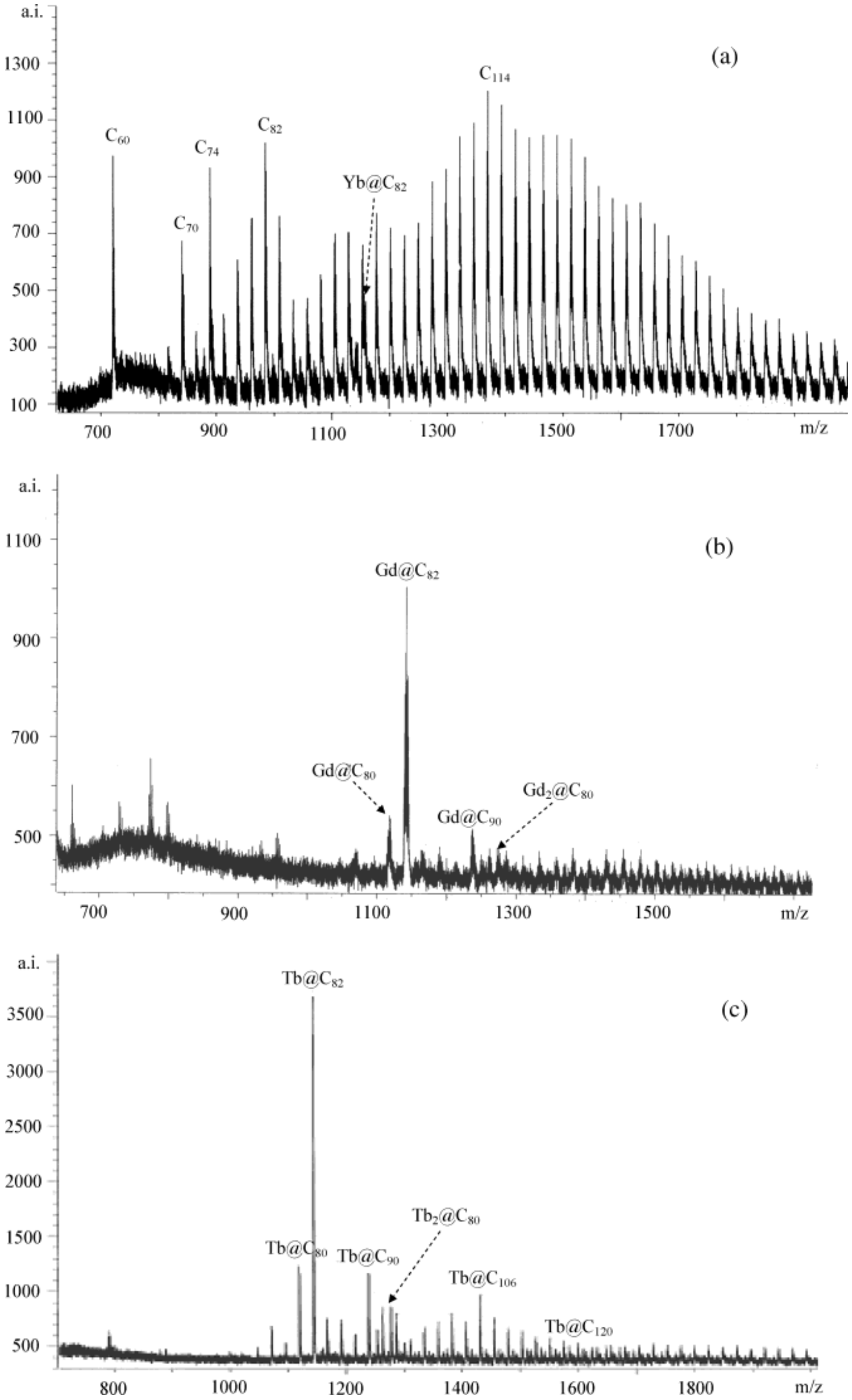

Figure 3. MALDI-TOF mass spectra of the DMF extracts containing (a) Yb, (b) Gd, and (c) Tb EMFs.

the content of Ca EMFs is about 10 times that of Yb or Ba ones. A similar phenomenon is also observed for trivalent EMFs. It can be seen from Figure 2 and Figure S2 that the relative intensity ratio $M@C_{82}$:C_{60} gets larger and larger when M changes from Gd, Y to Tb. Correspondingly, the number of extracted EMFs species is also increased.

Here, we should mention that it is unlikely to quantitatively evaluate the yield of any compounds on the basis of the mass-spectrum data. Because of the difference in photo ionization cross sections between empty fullerenes and EMFs, laser desorption and ionization in the mass spectral analysis discriminate the content of empty fullerenes such as C_{60} and C_{70} whereas they exaggerate that of varying EMFs. In the mass spectra of Tb EMFs containing samples, all strong peaks are originated from Tb EMFs whereas those owing to empty fullerenes including C_{60} and C_{70} are very weak. However, this does not mean that the content of Tb EMFs is also higher than that of C_{60} and C_{70}. In contrast, a much larger amount of empty fullerenes than EMFs were collected in our previous efforts on HPLC isolation.[14,24]

3.3. EMFs in DMF Extracts. Shown in Figure 3 are the MALDI-TOF mass spectra of DMF extracts containing (a) Yb, (b) Gd, and (c) Tb EMFs. Observed in Figure 3a are only prominent peaks from empty fullerenes, and those from Yb EMFs are hard to discern. Similar

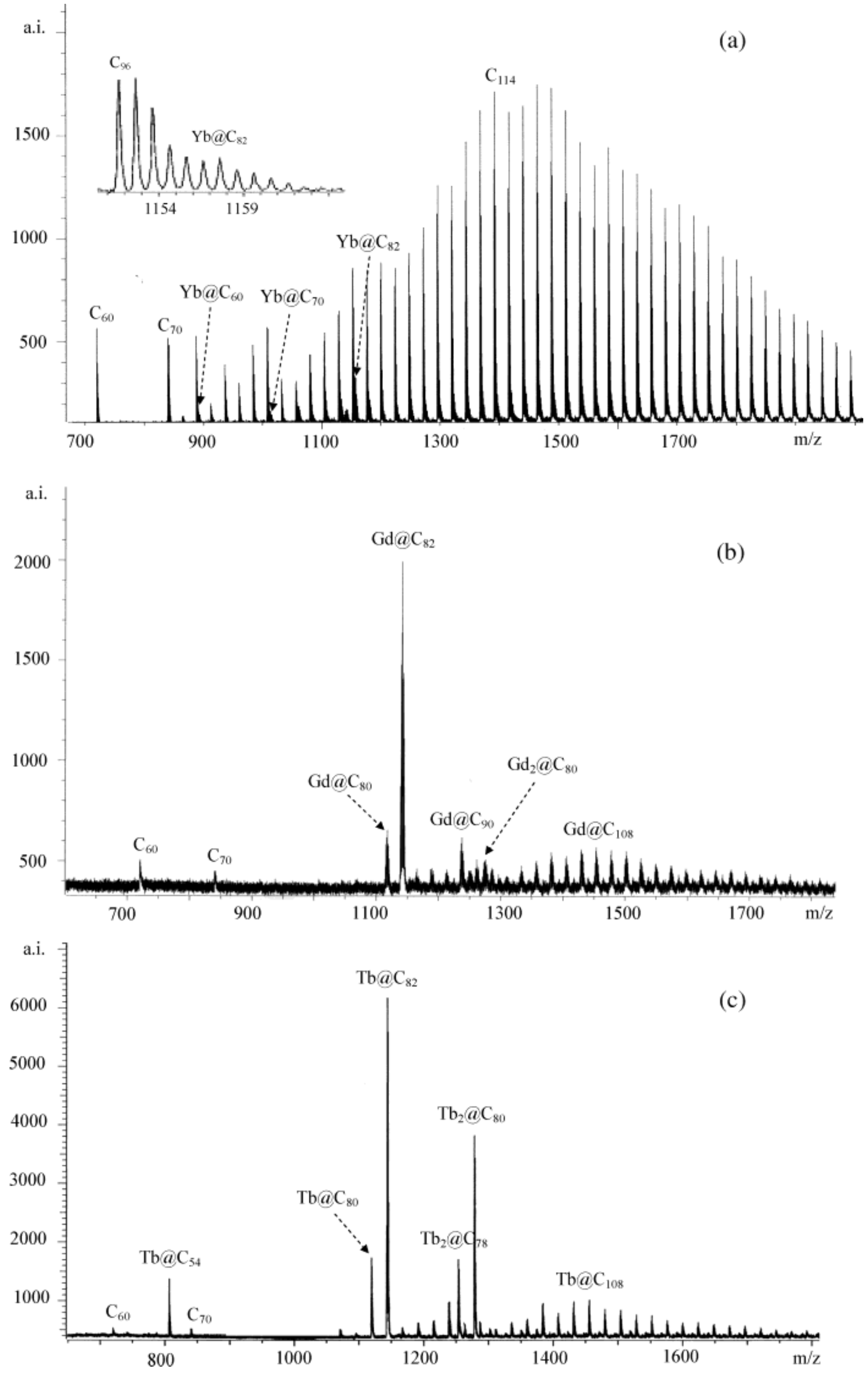

Figure 4. MALDI-TOF mass spectra of the pyridine extracts containing (a) Yb, (b) Gd, and (c) Tb EMFs.

features are also found in the mass spectra of DMF extracts of Ba, Ca, and Sm EMFs (see Figure S3). Thus, we think that DMF is not proper for further extracting divalent metallofullerenes from the carbon disulfide extraction residues. The poor extracting ability of DMF toward divalent EMFs leads Huang and Yang to conclude that the yields of Sm, Eu, Tm, and Yb EMFs are zero compared to that of $La@C_{82}$.[19]

It can be seen from Figures 3b and 3c that trivalent monometallofullerenes $M@C_{82}$, $M@C_{80}$, $M@C_{74}$, and $M@C_{90}$ as well as dimetallofullerenes $M_2@C_{78}$ and $M_2@C_{80}$ are selectively extracted by DMF from carbon disulfide extraction residues. Compared with previous work,[13] more species and higher content of EMFs with a minor amount of empty fullerenes are obtained. The low content of empty fullerenes in the extracts lies in two factors. First, the solubility of empty fullerenes in carbon disulfide is much higher than that of EMFs, and most of them are extracted out before subjecting to DMF extraction. Second, DMF has high selective extracting ability toward $M@C_{80}$, $M@C_{82}$, $M_2@C_{80}$, and other species.

3.4. EMFs in Pyridine Extracts. Figure 4 shows the MALDI-TOF mass spectra of pyridine extracts

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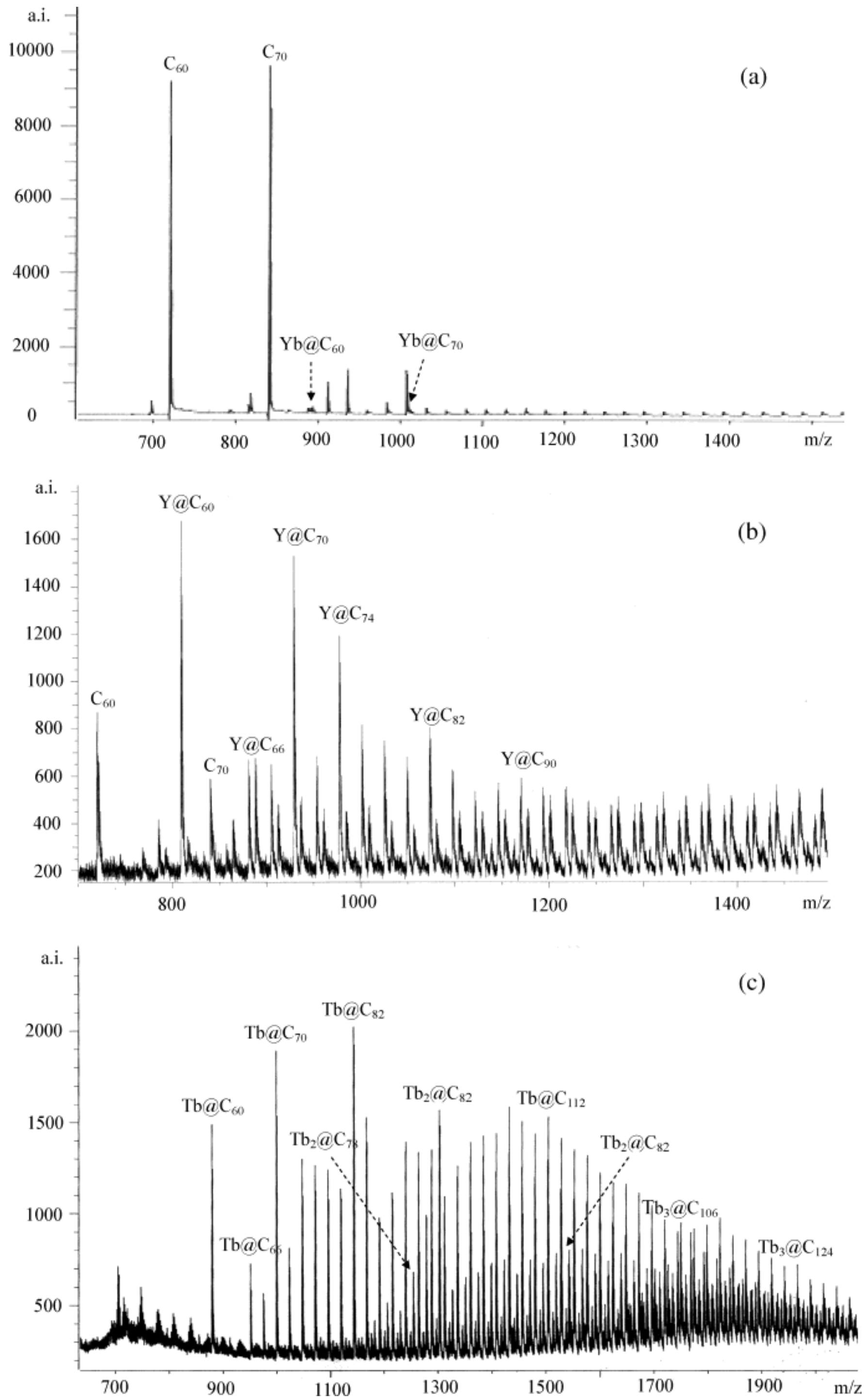

Figure 5. MALDI-TOF mass spectra of the aniline extracts containing (a) Yb, (b) Y, and (c) Tb EMFs.

containing (a) Yb, (b) Gd, and (c) Tb EMFs. The pyridine extraction behaviors of Yb EMFs are quite similar to Sm species reported previously.[5] Observed in Figure 4a are a series of combined peaks assignable to $Yb@C_{2n}$ ($2n = 60, 70-100$) and C_{2n+14}. Just as in the case of $Ca@C_{60}$ and $Ca@C_{70}$,[25] $Yb@C_{60}$ and $Yb@C_{70}$ are obviously extracted by pyridine, implying the special solubility of divalent C_{60}- and C_{70}-based metallofullerenes in pyridine. Considering the low preparation yield of divalent metallofullerenes, the extraction of pyridine toward divalent C_{60}- and C_{70}-based metallofullerenes is quite encouraging. From Figures 4b and 4c, it can be seen that pyridine shows similar extracting ability toward trivalent metallofullerenes; that is, $M@C_{80}$, $M@C_{82}$, $M@C_{90}$, and $M_2@C_{80}$ are selectively extracted. Moreover, a hunchbacked distribution in the peak intensity for monometallofullerenes is observed around the m/z of $M@C_{108}$ (M = Gd or Tb). Additionally, a peak appears at $m/z = 807$ with an intensity comparable to that of $Tb@C_{80}$ in Figure 4c. Because of its relatively strong intensity and no molecular ion peak assignable to $Tb_2@C_{108}$ ($m/z = 1614$) detected, this peak should neither be from second ion nor from the fragment of

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other metallofullerenes. Therefore, we tentatively ascribe it to Tb@C_{54}, which is of the smallest carbon cage among the extractable EMFs.

3.5. EMFs in Aniline Extracts. Figure 5 shows the MALDI-TOF mass spectra of aniline extracts containing (a) Yb, (b) Y, and (c) Tb EMFs. As shown in Figure 5a, only very weak peaks from EMFs such as Yb@C_{60} and Yb@C_{70} are identified, which can be ascribed either to the poor solubility of divalent EMFs in aniline or to the very low abundance of them in the residue after pyridine extraction. In contrast, a wide variety of yttrium monometallofullerenes Y@C_{2n} ($58 \leq 2n$) are clearly shown in Figure 5b, with the peak intensity of Y@C_{60}, Y@C_{70}, Y@C_{74}, and Y@C_{82} etc., nearly double their corresponding empty fullerenes. Compared with what was reported by Kubozono et al.,[12] many new species are found in our aniline extract, and the peak intensity ratios Y@C_{60}:C_{60} and Y@C_{70}:C_{60} are doubled along with higher peak resolution and better S/N (signal-to-noise). From Figure 5c we observed a series of monometallofullerenes Tb@C_{2n} ($2n = 60$, 66−158), dimetallofullerenes Tb_2@C_{2n} ($2n =$ 72−144), and trimetallofullerenes Tb_3@C_{2n} ($2n = 102$−132). Moreover, similar to the cases of raw soot and other three solvent extracts, the peak intensities of Tb EMFs are much higher than those of empty fullerenes in the mass spectrum of aniline extract, also suggesting a higher content of Tb EMFs both in the raw soot and in the solvent extracts than the other species of EMFs studied in this work. The difficulty in extraction of C_{60}- and C_{70}-based metallofullerenes was once ascribed to their instability in air or some common solvents.[4] Here, we evidenced that they are rather stable at atmosphere both in soot and in aniline solution.

4. Discussion

We would like to correlate the extraction behaviors of EMFs with the oxidation states of encaged metal atoms. For divalent metallofullerenes, only a series of monometallofullerenes M@C_{2n} (M = Sm, Yb, Ca and Ba; $2n \geq 72$), except a minor amount of Ca dimetallofullerenes, are extracted by carbon disulfide. As in the case of the raw soot, the peak intensity ratios M@C_{2n}:C_{60} found in the MALDI-TOF mass spectra are quite small, indicating their low content in the extracts. Among the extractable EMFs, M@C_{72} is always found to be of the smallest molecular weight among the extractable species and M@C_{84} constantly to be the most abundant in carbon disulfide extracts. Furthermore, the soluble divalent metallofullerenes are of comparable yield, which makes it possible for us to isolate a series of Sm monometallofullerenes.[24] Finally, C_{60}- and C_{70}-based monometallofullerenes can be extracted with pyridine or aniline.

For trivalent metallofullerenes, a series of mono-, di-, and trimetallofullerenes are extracted with carbon disulfide. In the case of monometallofullerenes, a distribution in abundance follows the order of M@C_{82} > M@C_{76} > M@C_{72} >M@C_{94} > M@C_{90}, and the content of other species, especially those based on higher fullerenes, is much lower than that of M@C_{82}. In line with the peak intensity ratios EMFs:C_{60}, we can conclude that the content of trivalent EMFs is much higher than that of divalent species. Both DMF and pyridine show high selective extracting ability toward M@C_{82}, M@C_{80}, M_2@C_{80}, and M@C_{90}, and C_{60}- and C_{70}-based metallofullerenes can only be extracted with aniline. Different from divalent EMFs, M@C_{66} is found to be of the smallest molecular weight among the extractable species and M@C_{82} exclusively to be the most abundant one in carbon disulfide, DMF, and pyridine extracts. Apart from Tb@C_{66}, we also observed peaks ascribed to La@C_{66} and La_2@C_{66} in the mass spectrum of carbon disulfide extract containing La EMFs.[20] Though high abundance of La@C_{66} and Tb@C_{66} are often observed in the mass spectra of their corresponding raw soot, we first extract monometallofullerenes based on the C_{66} cage. To date, isolation and structural characterization of C_{66}-based EMFs are limited to only Sc_2@C_{66}.[26] Because of its extremely low content in the raw carbon disulfide extract, Sc_2@C_{66} can only be attained after enormous enrichment efforts. Our success in extracting a few C_{66}-based metallofullerenes makes it possible to extensively study this novel type EMF.

It is meaningful to discuss the abundant distribution of multimetallofullerenes. A bulgy distribution in the peak densities of dimetallofullerenes is exclusively identified around the m/z of M_2@C_{100}. Nonetheless, the most abundant species is not in this range. According to Shinohara et al.,[27] Sc_2@C_{84} is the most abundant among a series of soluble Sc dimetallofullerenes. We show here that Y_2@C_{82} is the most abundant soluble Y dimetallofullerenes (see Figure S2). Moreover, lighter rare earths dimetallofullerenes M_2@C_{80} (M = La, Ce, Pr)[28−30] and those of heavier rare earths M_2@C_{82} (M = Dy, Ho Er)[31−33] have been isolated as the most abundant species. We argue that the carbon cage for the most stable rare earths dimetallofullerenes evolves from C_{80} via C_{82} to C_{84} as the metallic radius decreases. A similar trend is also observed for trimetallofullerenes. To date, the extracted and isolated trimetallofullerenes are limited to Sc_3@C_{82}, Ho_3@C_{82}, and Er_3@C_{82},[31−34] all of which are based on the C_{82} cage. We found here that Tb_3@C_{80} is the most abundant among a series of endohedral Tb trimetallofullerenes. A few years ago Stevenson et al.[35] reported synthesis of some trimetallic nitride EMFs, such as Sc_3N@C_{80} and Er_3N@C_{80}. When an extra nitrogen atom is encaged along with three Sc or Er atoms, the stable carbon cage changes from C_{82} to C_{80}. Further investigation on this phenomenon would be helpful for elucidating the formation mechanism as well as the electronic or symmetric structures of EMFs.

It has long been an open question on the oxidation state of scandium atom(s) inside carbon cages.[36−40] From

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the viewpoints of extraction behaviors, (1) a series of Sc multimetallofullerenes have been extracted; (2) the content of Sc@C_{82} is much higher than that of Sc@C_{84} and other monometallofullerenes in carbon disulfide extract; (3) a C_{66}-based dimetallofullereene Sc_2@C_{66} has been extracted and isolated.[26] Therefore, we believe that the Sc atoms inside the carbon cage are in the trivalent state, which is consistent with the recent results of the high-energy spectroscopy.[41] Further support comes from the HPLC isolation behaviors of M@C_{82}. According to Sueki et al.,[18] the retention time of Sc@C_{82} is similar to that of La-, Ce-, Gd-, Ho-, and Y@C_{82}, whereas that of Eu-, Tm-, and Yb@C_{82} is found to be a little shorter. Four isomers of Ca@C_{82}[42] and three isomers of Sm@C_{82}[24] and Tm@C_{82}[43] have been isolated to date, while only two structural isomers of Sc@C_{82}[44] have been produced and isolated, just as in the case of La@C_{82} and Pr@C_{82}.[45,46] Moreover, the major isomer of Sc@C_{82} is experimentally determined to have C_{2v} symmetry,[40] which is of the same molecular symmetry as the main isomer of La@C_{82} or Pr@C_{82},[47,48] but different from that of the main isomer of Tm@C_{82} (I) (C_s symmetry).[43] Since Sueki et al. pointed out that carbon cages for metal atoms of +2 oxidation state are not the stable cage for atoms of the +3 oxidation state,[49] it is reasonable for us to ascribe the oxidation state of scandium atoms encaged in a carbon cage as +3.

From the varying extraction behaviors of divalent and trivalent metallofullerenes outlined above, we conclude that the content and species multiplicity of EMFs are directly proportional to the electron number transferred from encaged metal atoms to carbon cages. Huang and Yang[19] correlated the relative yield with the charge transfer in metallofullerene molecule and the resulting effective dipole moments. They assumed that the metallofullerenes with higher relative yields might have a higher degree of charge transfer or a higher effective dipole moment. Because of one more electron transferred from encaged metal atoms to carbon cages, trivalent metallofullerenes should have higher preparation yields and higher effective dipole moments than divalent congeners, and hence have a better solubility in polar solvent. Therefore, some of them can be selectively extracted in high yield from the carbon disulfide extraction residues with polar solvents. In contrast, divalent metallofullerenes are expected to have a lower degree of charge transfer and then a lower effective dipole moment. Thus, they ought to have better solubility in weak polar solvents, and then most of them are extractable with carbon disulfide. Apart from the electrons transferred from metal atom to carbon cage, we should also pay our attention to the back-donation from the carbon cage. Lu et al.[50] proposed a strong hybridization between the d valence orbital of encaged rare earths and the carbon cage orbital. They found that through hybridization the unpaired electron is primarily demoralized on the cage but the occupied valence orbital contain significant d character. We argue that the varying degree of such back-donation leads to the different extraction behaviors within the divalent or trivalent groups. For example, among the trivalent metallofullerenes studied in this work, Nd EMFs have the lowest content. Moreover, we are not sure of the existence of Nd multimetallofullerenes because of the coincidence in atomic weight between neodymium and carbon. We ascribe the relatively low content of Nd EMFs to the considerable back electron donation from carbon cage to Nd atom. This postulate is supported by the theoretical predictions made by Kobayashi and Nagase,[51] who suggested the electronic structure of Nd@C_{82} to be described formally as Nd^{2+}@C_{82}^{2-} because of great back electron donation. As for the exceptionally high yields of Tb EMFs, Huang and Yang[19] attributed it to the facile formation of metal−carbon cluster $(TbC_2)_n$ at high temperature, which is supposed to be the metallofullerene precursors. In our opinion, because of its special electronic structure ($4f^96s^2$), the Tb atom might transfer 4 electrons to carbon cages to form half-filled structure with large back-donation or transfer 3 electrons with small back-donation. Therefore, the net amount of electrons transferred from Tb atom to carbon cage is larger than that from other rare earths, which is responsible for the high content and the species multiplicity of Tb EMFs in the solvent extracts.

The selective extraction of DMF and pyridine toward M@C_{82}, M@C_{80}, and M_2@C_{80} and aniline toward M@C_{60} and M@C_{70} might be elucidated on the basis of a solvent reduction process. La@C_{82} is a proper example to this target. It is well-known that La@C_{82} has an open-shell structure because of a three-electron transfer from La to the C_{82} cage. Addition of one electron leads to La@C_{82}^- anion, which has a closed-shell electronic structure owing to the full occupation of the singly occupied LUMO+1 level of La@C_{82}. The solvent dependence of the electrochemistry of fullerene has been recorded. The reduction potential of C_{60}/C_{60}^- changes from −1.12 V in 1,2-dichlorobenzene[52] to −0.312 V in DMF, −0.343 V in pyridine, and −0.396 V in aniline,

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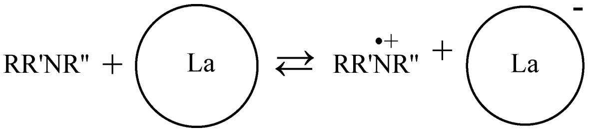
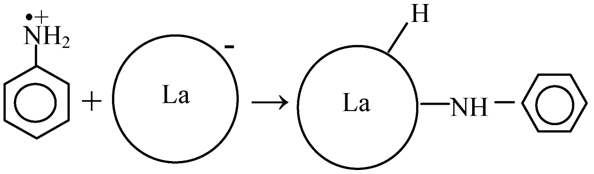
repectively.[53] The reduction potential of La@C_{82}/La@C_{82}^- is −0.42 V in 1,2-dichlorobenzene,[52] which should increase to a much more positive value in amino solvents. This means that La@C_{82} is a stronger electron acceptor than C_{60}. On the other hand, it is well-known that monoanion radicals, C_{60}^- and C_{70}^-, could be formed when fullerenes C_{60} and C_{70} react with amines and their derivatives.[54,55] Furthermore, soluble anions of small band gap fullerenes and Gd-metallofullerenes including Gd@C_{60} and Gd@C_{70} were obtained by chemical and electrochemical reduction.[56,57] Recently, Solodovnikov et al.[58] proved the formation of La@C_{82}^- anion when La@C_{82} dissolved in DMF or pyridine by optical and electron paramagnetic resonance spectroscopy. Thus, it would be reasonable for us to discuss the EMF extraction behavior on the basis of the solvent reduction process.

The three nitrogen-based solvents function as organic reducing agents. One-electron transfer from DMF, pyridine, or aniline (denoted as RR′NR″) to La@C_{82} gives La@C_{82}^- anion and solvent radical cation.



(1)

Fullerenes and carbon nanotubes have been shown to form donor−acceptor complexes with aniline and substituted anilines.[59,60] Analogously, upon recombination La@C_{82}^- anion and radical aniline cation form a charge-transfer complex, which is followed by proton transfer from aniline to La@C_{82}.



(2)

EMF-aniline complex is quite stable, and the EMFs could not be returned back to neutral form by evaporation of the solvent. In contrast, the N atoms in DMF^+ and Py^+ (Py = pyridine) are inaccessible for covalent binding to EMF, and the formation of complex by proton transfer from DMF or Py to EMF is impossible. Since reaction (1) is reversible, neutral EMFs would be obtained by evaporation of the solvents. Therefore, the EMFs extracted with DMF and pyridine, after evaporation of solvents, can be dissolved again in toluene for further HPLC isolation.

5. Conclusions

We systemically investigated the extraction behaviors of some EMFs with a continuous four-step extraction procedure. Among the organic solvents employed in this work, carbon disulfide shows a special extracting ability toward a series of divalent monometallofullerenes and trivalent multimetallofullerenes, which is mainly owing to the resemblance in weak polarity between the solvent and the EMFs. DMF and pyridine demonstrate selective extracting power toward trivalent metallofullerenes such as M@C_{82}, M@C_{80}, M_2@C_{80}, and M@C_{90}. The relative high content of the above species in DMF and pyridine extracts evidences the incompleteness of carbon disulfide extraction. Moreover, pyridine is also proved to be an effective solvent to extract divalent metallofullerenes such as M@C_{60}, M@C_{70}, and M@C_{84}. In contrast, C_{60}- and C_{70}-based trivalent metallofullerenes can only be extracted with aniline. The varying extraction behaviors between divalent and trivalent EMFs can be explained on the basis of the transformed electrons from the encaged metal atoms and the back-donation from carbon cages. To clarify the special extraction selectivity of DMF, pyridine, and aniline toward certain EMFs, a detailed solvent leading reduction of EMFs is proposed.

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Supporting Information Available: The other MALDI-TOF mass spectra of the endohedral metallofullerenes studied in this work (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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