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Recent progress in the studies of endohedral metallofullerenes

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Abstract

This overview presents the recent progress in the area of endohedral metallofullerenes in the past several years. The important results have been summarized as follows: (1) Many metals including Group 3 metals, most of the lanthanide series elements, and Group 2 metals have been encapsulated into a fullerene cage to form mono-, di-, and trimetallofullerenes by using the arc-evaporation technique. (2) Some endohedral metallofullerenes such as Group 3 metals, most of the lanthanide series elements, Group 2 metals, and some of their isomers have been successfully isolated and purified by a two-step or several-step HPLC technique. By using high-temperature and high-pressure extraction with pyridine, Ln@C_{80}, Ln@C_{82}, and Ln_2@C_{80} for most rare-earth metals have been selectively extracted in high yield (about 1% of the raw soot) from fullerenes and other size metallofullerenes. (3) The endohedral nature of metallofullerenes such as Y@C_{82}, Sc_2@C_{84}, and Sc@C_{82} has been finally confirmed by synchrotron X-ray powder diffraction. The symmetries and the structures of metallofullerenes such as Ca@C_{82}(III), La_2@C_{80}(I_h), Sc_2@C_{84}(D_{2d}), and Sc_2@C_{84}(C_s) have been confirmed by NMR measurements. (4) The information on the electronic structures and properties of endohedral metallofullerenes has been obtained by various spectrometric means such as EPR, UV–vis–NIR, XPS, CV. It is generally accepted that three-electron transfer is favorable when M = Y, La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, Lu but Sc, Eu, Sm, Yb, Tm, Ca, Sr, Ba prefer to donate two electrons to the fullerene cages. (5) Several chemical reactions of endohedral metallofullerenes have been reported in which reagents are disilacyclopropane, digermacyclopropane, diphenyldiazomethane, and trifluoroacetic acid. (6) Mass spectrometry provided the crucial evidence that led to the discovery of metallofullerenes in 1985 and has always played a key role in their identification and characterization. Ion-mobility measurements of gas-phase ions have obtained the information of structures and the formation mechanism of endohedral metallofullerenes. (7) Theoretical calculations on the endohedral metallofullerenes have made an important contribution to the studies on the symmetry of the cage, the position of metal atom(s) inside the cage, the number of electronic transfer between metal atom(s) and fullerene cage, etc.

Keywords: Endohedral metallofullerene; Synthesis; Isolation; Structure; Property

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1. Introduction

During the last few years, considerable progress has been made in the exploration of metallofullerene chemistry especially that of endohedral [1–3]. As is well known, fullerenes have a unique type of inner empty space with their unusual cage-like structures. A wide variety of metal atoms may reside in this space and form endohedral metallofullerenes. These new series of materials with novel physical and chemical properties are very important for their potential application as new types of superconductors, organic ferromagnets, nonlinear optical materials, functional molecular devices, magnetic resonance imaging agents, and biological tracing agents, etc., which will have great influence over electronics, optics, electromagnetics, and medicine.

In 1991, Chai et al. [4] reported the first macroscopic amount of metallofullerenes by laser vaporization of a graphite–metal composite in a helium-filled tube-oven at high temperature. Subsequently, great efforts have been made for the production and characterization of endohedral metallofullerenes. Up to now, many metals including Group 3 metals (M = Sc, Y, La), most of the lanthanide series elements, Group 2 metals (M = Ca, Sr, Ba), alkali metals (M = Li, Na, K, Cs), and some tetravalent metals (M = U, Zr, Hf) have been success-

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fully encapsulated into a fullerene cage to form mono-, di-, and trimetallofullerenes. Especially, the important progress has been marked by the successful isolation and purification of many metallofullerenes and their isomers, which has led to further investigation of their molecular structures, physical and chemical properties as well as electronic states by a variety of experiment means, especially that of spectroscopy. The endohedral nature of metallofullerenes such as $Y@C_{82}$, $Sc_2@C_{84}$, and $Sc@C_{82}$ has been finally confirmed by synchrotron X-ray powder diffraction [5–7]. The information on the electronic structures and properties of endohedral metallofullerenes has been obtained by various spectroscopic methods such as EPR, UV–vis–NIR, XPS, CV. Meanwhile, theoretical studies of endohedral metallofullerenes have made an important contribution and the symmetry of the cage, the position of metal atom(s) inside the cage, the number of electronic transfers between metal atom(s) and fullerene cage, etc., have been calculated.

However, because of the extreme difficulty in producing samples in quantities greater than a few 100 mg, thorough investigation of metallofullerenes has been hampered, so their chemical properties have been little studied. A definitive structure proof has not been performed for some series of endohedral metallofullerenes, and the theoretical studies do not always agree with the experimental results. These questions will be solved with the availability of pure samples in a greater quantity.

In this account, we summarize recent progress in the studies of endohedral metallofullerenes in an attempt to understand overall, the important properties of these novel compounds.

2. Synthesis and isolation

Synthesis and isolation of endohedral metallofullerenes has attracted considerable interest because they are very important for further investigation of physical and chemical properties, molecular structures, and some interesting applications of metallofullerenes. Since the improvement of synthetic methods by Krätschmer et al. in 1990 [8], a great deal of work has been done to produce endohedral metallofullerenes.

The synthetic methods of endohedral metallofullerenes are in principle identical to that employed for the synthesis of empty carbon cages. The main method is the arc-evaporation technique in which the arc burns a composite rod made from a metal oxide and graphite in a depressurized He gas. Prior to arc-burning, the composite rod is normally subjected to heat treatment and carbonation at high temperature in a high vacuum. It is believed that the composed metal oxide has been changed to the metal carbide in the heat treatment. The soot produced contains numerous metallofullerenes and empty fullerenes in which some species of metallofullerenes are relatively stable and soluble, to allow extraction with solvents such as pyridine, toluene, and carbon disulphide. Their solubilities are similar to those of giant fullerenes, dissolving better in carbon disulphide and pyridine than in toluene [9,10]. In addition, Huang et al. [11] reported a new route to incorporate La atoms inside the fullerene cages by way of laser vaporization and excitation of fullerene C_{60} and La in a mixture of C_{60} and La_2O_3, which provided the first evidence for endohedral metallofullerene formation by letting atoms penetrate into the empty carbon cage through a sort of ‘opening window’ mechanism. Monolayers of C_{60} are exposed to an intense beam of alkali ions at an energy chosen so that the ions can also penetrate the carbon cage but cannot destroy it [12]. With this new ‘opening window’ reaction, synthesis of metallofullerenes has become a realistic expectation. Endohedral metallofullerenes containing yttrium atoms were also produced by laser irradiation of a mixture of graphite and Y_2O_3 target [13].

Production of endohedral metallofullerenes is generally inefficient, the yield is normally below 1% from the original soot, and is limited in part by the reactivity and scant solubility of metallofullerenes. Production efficiency and the species of metallofullerenes increase if metal carbides are used as metal sources [14], or if the carbide-rich cathode deposit produced in situ during arc-vaporization is ‘back-burned’ by reversing the arc polarity. The yield of the lanthanofullerene $La@C_{82}$ has increased by a factor of 10 or more when LaC_2-enriched composite carbon rods are used for the generation of soot [15]. The part of metallofullerenes (especially multiple-metal fullerenes) increases with increasing metal–oxide loading [16]. If the ratio is approximately 1 La/100 C atoms, only $La@C_{2n}$ species are observed; however, if the ratio is raised to nearly 2 La/100 C atoms, the $La_2@C_{80}$ signal appears in the mass spectrum. Anaerobic techniques also improve the yield of some endohedral metallofullerene species [17]. Saito et al. [18] reported a He buffer pressure dependence of the yield of $La@C_{82}$ during the arc synthesis by using electron spin resonance (ESR). It is found that the production of two structural isomers of $La@C_{82}$ (I and II) attains maximum yield around 200 Torr.

In addition, the yield of endohedral metallofullerenes has been found to depend significantly on the metal species and properties. A semi-quantitative analysis of the relative yields for Group 3 elements revealed that La gives the highest yield and Y the second, while Sc gives the lowest yield [19]. Similar results have also been suggested by Ross et al. [9]. This result could be attributed to greater abundance of metallofullerenes containing the lower ionization potential metal atom (IPs of La, Y, Sc are 5.58, 6.2, 6.54 eV). However, the yields of $Sr@C_{84}$ and $Ba@C_{84}$ are about 70 and 20% of that of $Ca@C_{84}$ (isomer I), respectively [20]. The larger size of the Ba^{2+} could explain the lower absolute yield of Ba-metallofullerenes, as compared to Ca- and Sr-metallofullerenes. In our previous study [21], the yields of Sm-, Eu-, Yb-, and $Tm@C_{82}$ (M possessing +2 oxidation states) are much lower than those of other rare earths with +3 and +4 oxidation states. The size of hollow fullerenes that contribute to the formation of monometallofullerenes has been demonstrated to have a strong selectivity. In this case, the C_{82} fullerene has been found to have a particular ability to form metallofullerenes possessing the properties of air resistance and extractability.

The isolation and purification of samples proved to be a major experimental challenge due to the small quantities of metallofullerenes generated, coupled with their similarity in size and shape to empty fullerenes. The complete separation is barely possible by conventional methods. Purified samples did not become available until milligram quantities of $La@C_{82}$ were isolated in 1993 by two-step HPLC [17,22]. Since then, many endohedral metallofullerenes have been isolated and purified by a variety of methods (see Table 1).

Furthermore, Xiao et al. [40] developed a method by which $M@C_{82}$ (M = La, Y) were separated from metal-free fullerenes in a single step. They employed silica-packed HPLC columns in which tetraphenylporphyrin moieties are anchored to the silica surface through carboxyl groups. The three-dimensional interaction between the silica-anchored porphyrin and the fullerenes provides a plausible explanation for the unusual selectivity of this stationary phase for fullerenes and metallofullerenes. The lanthanofullerene $La@C_{82}$ was also isolated by an efficient single-stage chromatographic separation process with pyrenylethyl–silica as a stationary phase [41]. The direct coupling of HPLC with the on-line EPR technique is clearly advantageous in the investigation and chromatography of labile and/or air-sensitive samples [42].

Table 1
Isolated and purified endohedral metallofullerenes

M	$M_m@C_{2n}$
Group-3-based	$Sc_2@C_{84}$(I), $Sc_2@C_{84}$(II), $Sc_2@C_{84}$(III), $Sc_2@C_{74}$, $Sc_3@C_{82}$, $Sc_2@C_{82}$(I), $Sc_2@C_{82}$(II), $Sc_2@C_{86}$(I), $Sc_2@C_{86}$(II), $Sc_2@C_{76}$, $Y@C_{82}$, $La_2@C_{80}$, $La@C_{82}$(I), $La@C_{82}$(II) [23–28,32,33,37]
Lanthanide	$Ce@C_{82}$, $Ce_2@C_{80}$, $Pr@C_{82}$, $Pr_2@C_{80}$, $Nd@C_{82}$, $Sm@C_{82}$(I), $Sm@C_{82}$(II), $Sm@C_{82}$(III), $Sm@C_{74}$, $Sm@C_{84}$, $Eu@C_{74}$, $Gd@C_{82}$, $Dy@C_{82}$, $Ho_2@C_{82}$, $Er_2@C_{82}$, $Er@C_{82}$, $Tm@C_{82}$(I), $Tm@C_{82}$(II), $Tm@C_{82}$(III), $Yb@C_{82}$(I), $Yb@C_{82}$(II), $Yb@C_{82}$(III), $Yb@C_{84}$ [28–35]
Group-2-based	$Ca@C_{82}$(I), $Ca@C_{82}$(II), $Ca@C_{82}$(III), $Ca@C_{82}$(IV), $Ca@C_{72}$, $Ca@C_{74}$, $Ca@C_{84}$(I), $Ca@C_{84}$(II), $Ca@C_{80}$, $Sr@C_{82}$, $Sr@C_{84}$, $Sr@C_{80}$, $Ba@C_{84}$, $Ba@C_{80}$ [36–39]

Although the availability of new chromatographic methods has helped to overcome the problem of isolation of endohedral metallofullerenes, their production is still very difficult and the sample quantities are often in the milligram range. The preparation of milligram amounts of purified samples is still very time consuming and solvent consuming. Stevenson et al. [43] devised an automated HPLC system for relatively large-scale separation of the metallofullerene fractions, which allows separation of 125–200 mg of metallofullerene-containing extract in a 16 h time period.

In our previous studies, rare-earth metallofullerenes can be efficiently extracted from the insoluble part of the soot after toluene Soxhlet extraction by way of the high-temperature and high-pressure extraction with pyridine [44–46]. By using this method, $Ln@C_{80}$, $Ln@C_{82}$, and $Ln_2@C_{80}$ for most of the rare-earth metals have been selectively extracted in high yield (about 1% of the raw soot) from fullerenes and other size metallofullerenes in a closed vessel under inert gas protection (see Fig. 1). Why is this method effective? First of all, it is reasonable to believe that the solvation of metallofullerenes is an endothermic process, high-temperature would be favorable to the further solvation of metallofullerenes. Secondly, the polarity of the solvent is another important factor governing extraction efficiency. The encapsulating of the metal ion enhances the molecular polarity of $M@C_{2n}$, which makes $M@C_{2n}$ more soluble in the polar solvent pyridine. High-temperature, high-pressure extraction with toluene has also proved to be effective for the extraction of $Gd@C_{82}$and $La@C_{2n}$ [47–49]. Ding and Yang [50] have successfully developed an efficient extractive scheme to separate metallofullerenes, which selected DMF to be preferentially extracted from raw soot. After removal of DMF by evaporation, a soluble fraction of the black powder was dissolved in toluene and injected into an HPLC system. This made it possible for single-step HPLC separation of metallofullerenes such as $Ce@C_{82}$, $Ce_2@C_{80}$, $Nd@C_{82}$, $Pr@C_{82}$, to be obtained with ~99.5% purity. Recently, we have also obtained a similar experimental result and isolated metallofullerene $Gd@C_{82}$ (see Fig. 2) [51]. In addition, the enhancement of extraction efficiency of metallofullerenes can be obtained by mixing the dipolar solvent CH_3OH with CS_2 [52]. Yeretzian et al. [53] published an experimental result that metallofullerenes were separated and enriched by using a gradient sublimation method.

In the studies on endohedral metallofullerenes, most works have focused on $M@C_{82}$, $M@C_{80}$, and $M@C_{74}$ except a few on $M@C_{60}$; the slower progress in studies

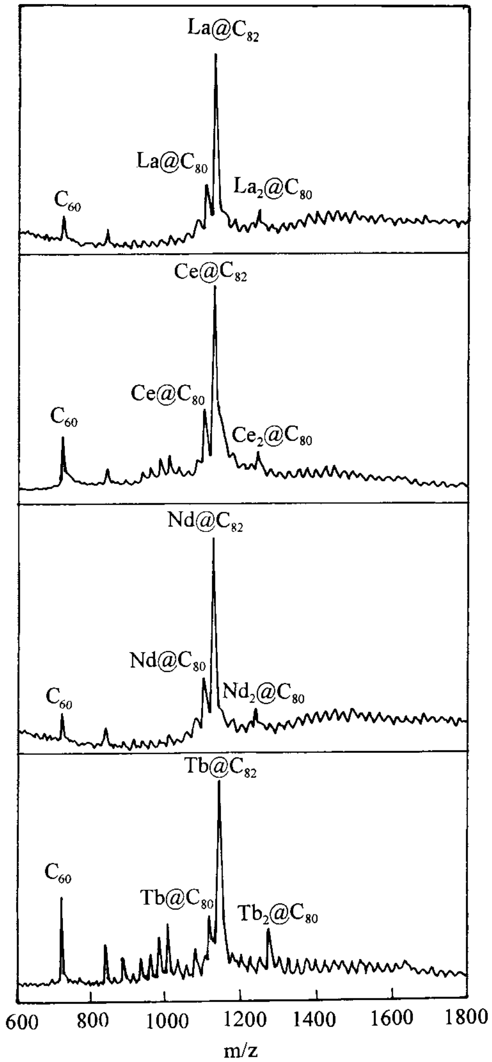

Fig. 1. LD mass spectra of pyridine high-temperature, high-pressure extracts obtained from soot produced by the arc-burning of carbon rods containing the rare-earth oxides La_2O_3, CeO_2, Nd_2O_3 and Tb_4O_7. Ln@C_{80}, Ln@C_{82} and Ln_2@C_{80} of each element can be observed with high intensity, indicating that they have been extracted in high yield from the soot.

of M@C_{60} can be attributed to the difficulty of its extraction. Kubozono et al. [54,55] found that aniline is a suitable extraction solvent for M@C_{60}; Y@C_{60}, La@C_{60}, Ce@C_{60}, Pr@C_{60}, Nd@C_{60}, Gd@C_{60}, Ca@C_{60}, Sr@C_{60} and Ba@C_{60} were extracted successfully with aniline under an air atmosphere.

Up to now, many metals in the Periodic Table have been encapsulated into a fullerene cage. Metallofullerenes containing up to three or four metal atoms in the cage have been observed [56]. Although the smaller size endohedral metallofullerenes have not yet been isolated in macroscopic amounts, mass spectroscopy has indicated that some species may be very stable, in particular M@C_{28} (M = U, Zr, Hf) [57]. The metal atoms were made radioactive by a neutron-capture reaction or through a nuclear-decay process [58–61]. The intriguing finding is that the endohedral form of metallofullerenes is not affected by the recoil energy of the metal atom resulting from emission of electrons in the decay. Successful encapsulation of radioactive atoms inside the fullerene cage will greatly widen the potential use of endohedral metallofullerenes not only in basic science but also in other fields, such as medicine.

3. Structure and isomerism

Since the idea that fullerene cages could accommodate metal atom(s) inside was proposed, a large amount of study on the endohedral nature of metallofullerene has been performed. Although there has been some debate about this problem, observations by means of electron spin resonance (ESR), extended X-ray absorption fine structure (EXAFS) [62], scanning tunneling microscopy (STM) [63,64], transmission electron microscopy (TEM) [65], and especially synchrotron powder X-ray diffraction have strongly suggested that the metal atom(s) are indeed inside the fullerene cages. Theoretical calculations also support this viewpoint [66,67]. In the studies of ESR for Sc_3@C_{82} [68–71], the symmetric hyperfine splitting of the 22 lines indicates that the three scandium ions must be equivalent and trapped inside the C_{82}, which is consistent with the structure of Sc_3@C_{82} having C_{3v} symmetry. Three Sc ions form an equilateral triangle in the cage or move rapidly to give equivalence on the time scale of the ESR experiment. STM and TEM studies were also carried out in an attempt to confirm metal atom(s) are inside the fullerene cages. Shinohara et al. [63] reported the direct, real space images of the purified Sc_2@C_{84} by utilizing STM. The STM images of the Sc_2@C_{84} show

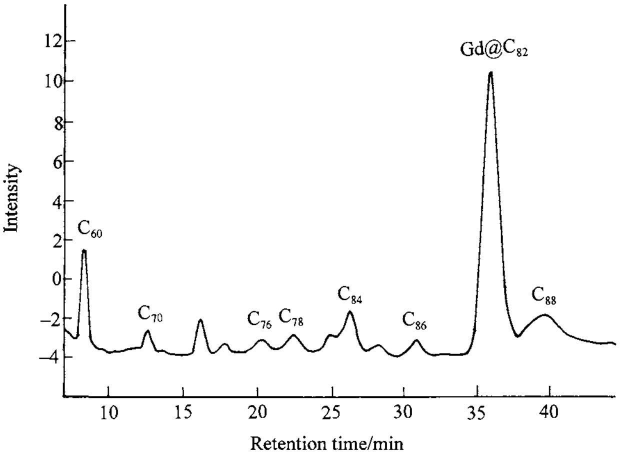

Fig. 2. HPLC chromatogram of the endohedral metallofullerene Gd@C_{82} collected from the toluene solution of the concentrated DMF extract. Gd@C_{82} can be observed with high intensity, indicating that the solubilities of empty fullerenes C_{2n} in polar solvent DMF is limited and the solubility of endohedral metallofullerene Gd@C_{82} is favorable to DMF.

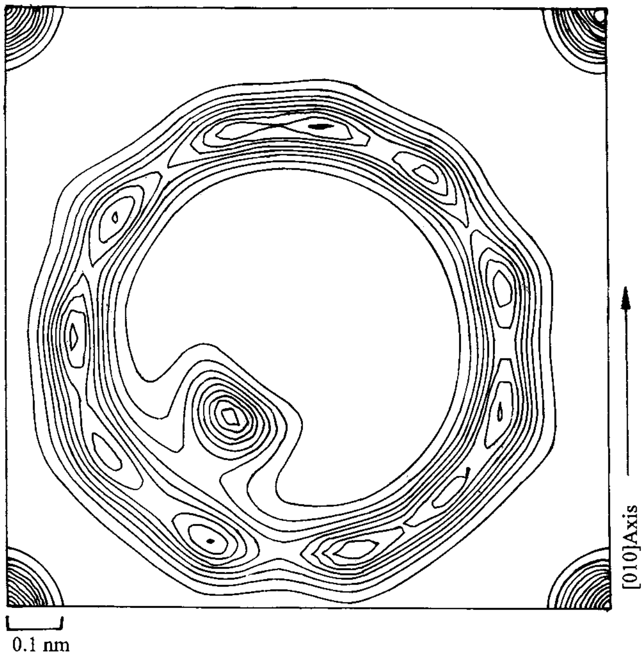

Fig. 3. The MEM electron density distribution of Sc@C_{82} (from Ref. [7]). For metallofullerene Sc@C_{82} there are remarkably high densities just inside the C_{82} cage. Evidently, the charge density maximum at the interior of the C_{82} cage represents the Sc atom, indicating that the metal position is off center and the Sc atom is indeed inside the C_{82} cage.

no characteristic bright (or dark) spot (which may correspond to the position of Sc atoms) on and around the carbon cage and individual Sc_2@C_{84} molecules are imaged to be spherical. From the image it can be seen that the nearest-neighbor distance of the Sc_2@C_{84} molecules (11.7 Å) is slightly smaller than that of the hollow C_{84} molecules (12.0 Å). Lately, similar results were also obtained by Wang et al. [72] in the investigation of Sc@C_{74} and Sc_2@C_{74}. Furthermore, the combination of the maximum entropy method (MEM) and the Rietveld refinement from synchrotron powder diffraction data is a powerful means for determining the endohedral nature of metallofullerenes. By using this method, the endohedral nature of Y@C_{82} was finally confirmed by Takata et al. [5] in 1995. For Y@C_{82} there are remarkably high charge densities just inside the C_{82} cage, whereas there is no such high-density region in C_{82}. The number of electrons around the maximum is about 38, which is very close to the atomic number of an Y atom. Evidently, the charge density maximum at the interior of the C_{82} cage represents the Y atom. Recently, Nishibori et al. [7] obtained very similar experimental results in studies of Sc@C_{82} by the MEM method (see Fig. 3).

Since there are many isomers for endohedral metallofullerenes, the determination of structures and symmetries has long been a fundamental interest in disclosing a mechanism of growth. It seems likely that cage-like structures with a metal atom inside are formed through several steps (monocyclic rings–cycloadducts–hoops–closed fullerene cages), as discussed for fullerene formation. In many cases, the initial cages do not correspond to the stable structures; however, they are able to isomerize to find stable structure during the annealing process, because the overall process is highly exothermic. This is the reason why energetically stable structures are produced as the major isomer. The agreement between theoretical prediction and experimental results gives support to the view that energetically stable structures with a large HOMO–LUMO gap are abundantly produced [73,74]. Up to now, some metallofullerenes such as M@C_{82}, La_2@C_{80} and Sc_2@C_{84} have been extensively investigated from the experimental and theoretical points of view.

3.1. M@C_{82} (M = La, Y, Sc)

The observation of a single peak in the mass spectrum, but two octets for La@C_{82} in the ESR spectrum, suggested two different conformations of the same metallofullerene molecule [75]. Analysis of the temperature dependence of the electron-spin relaxation times indicated that there was a thermal equilibrium between the two configurations [76]. In addition, from ESR spectra, two species with ratios of about 0.07 for Sc@C_{82}, 0.15 for Y@C_{82}, and 0.27 for La@C_{82} were found [77]. Later, more careful extraction under anaerobic conditions gave five different octet species; among them, two La@C_{82} species are relatively stable molecules [78]. It is proposed that M@C_{82} does not exist as a single species in solution, but as several isomers possessing either different cage structures or different metal positions, or form adducts with hollow-fullerene molecules.

For the C_{82} fullerene, there are nine isomers which satisfy the so-called isolated pentagon rule [79]. The calculations show that the symmetry $C_2(a)$ is the most stable [80]. It seems plausible to assume that M is likely encapsulated inside the most stable $C_2(a)$ fullerene cage. In recent theoretical studies for Ca@C_{82} [81], however, it is highly destabilized by accepting two electrons and becomes the second most unstable for C_{82}^{2-}. Instead the C_{2v}, $C_s(c)$, $C_2(c)$ and $C_{3v}(c)$ cages, which are highly unstable for C_{82}, are drastically stable for C_{82}^{2-}. These four cages are close in energy for C_{82}^{2-}. This is remarkable since four isomers have been isolated and purified for Ca@C_{82} [36]. John et al. [82] have measured successfully the ^{13}C-NMR spectrum for one of the four Ca@C_{82} isomers. A total of 41 distinct lines with almost equivalent intensity have been observed. This agrees with structure Ca@C_{82}(III), which has 41 nonequivalent carbons and C_2 symmetry. However, the one-dimensional ^{13}C-NMR measurement alone cannot identify the final cage structure. A recent ab initio calculation on Ca@C_{82} shows that the most probable

C_2 isomer is the calcium atom being located along the C_2 axis. So NMR spectroscopy is one of the most useful structural probes.

Surprisingly, M@C_{82} with trivalent metal atom seems to form two dominant isomers such as La@C_{82} and Y@C_{82}, whereas M@C_{82} with divalent metals have been encapsulated in more than two cage isomers such as three isomers for Tm@C_{82} and four isomers for Ca@C_{82} [83,84,36]; these isomers have been separated by chromatography. For example, Kirbach and Dunsch [83] obtained three stable isomers Tm@C_{82}(A), Tm@C_{82}(B) and Tm@C_{82}(C) by the two-step HPLC separation method. The solution color of these isomers in toluene differs remarkably even at similar concentration, e.g. the solution of Tm@C_{82}(A) is green, that of Tm@C_{82}(B) yellowish–brown and that of Tm@C_{82}(C) brown–red.

The calculations show that M is located at the off-center position in M@C_{82} [85,86]. It is highly stabilized when M approaches the center of one hexagonal ring along the C_2 axis, regardless of the species of M (see Fig. 4). This is consistent with the EXAFS studies of Y@C_{82} [62] and La@C_{82} [87], which showed that the number of the nearest neighbor carbons is six. The calculated distance between M and hexagonal carbon is 2.464–2.477 Å for Y@C_{82}, which is in good agreement with the value of 2.4 Å evaluated from the EXAFS study. In addition, the density map from synchrotron X-ray diffraction [5] revealed that Y is displaced from the center of C_{82}. The Y–C distance of 2.47 Å is in almost-perfect agreement with the calculated value. In studies with the two-dimensional EPR spectrum for La@C_{82}, the non-vanishing value of the quadrupole interaction is further proof for an off-center position of the metal ion [88].

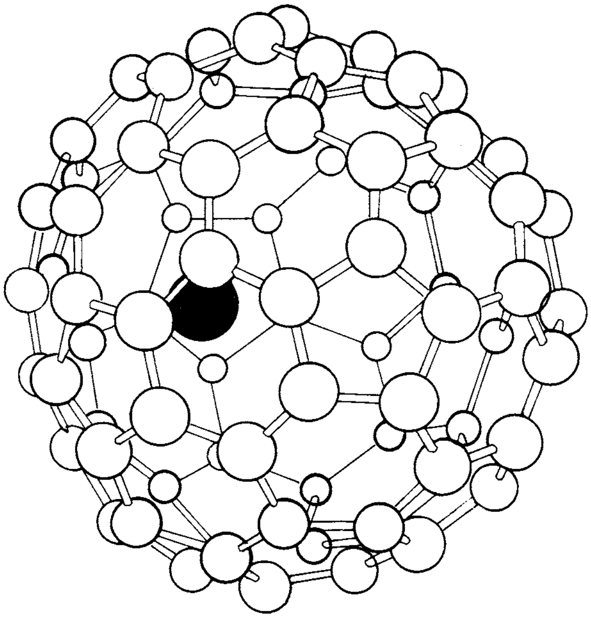

Fig. 4. The view of the $C_2(a)$ endohedral structure of M@C_{82}. The calculations show that M is located at the off-center position in M@C_{82}. It is highly stabilized when M approaches the center of one hexagonal ring along the C_2 axis, regardless of the species of M.

3.2. La_2@C_{80}

Two metal atoms can even be encapsulated inside the higher fullerene cages to form extractable and relatively air-stable endohedral metallofullerenes. Among these, La_2@C_{80} has obtained special interest as a representative and abundant dimetallofullerenes.

For the C_{80} fullerene, there are seven isomers which satisfy the isolated pentagon rule [79]. It seems plausible to assume that two La atoms are encapsulated inside the most stable D_2 or isoenergetic D_{5d} isomer. However, theoretical calculations have predicted that the I_h isomer of C_{80} should be able to accommodate two La atoms to form a thermodynamically and kinetically stable metallofullerene. This is because the I_h–C_{80} has only two electrons in the fourfold degenerate HOMO and can accommodate six electrons from two La atoms to form the stable, closed-shell electronic state of $(La^{3+})_2C_{80}^{6-}$ with a large HOMO–LUMO gap [89]. The two La atoms are located equivalently on the C_2 axis facing the hexagon rings of $C_{80.}$ Confirmation of I_h symmetry for La_2@C_{80} has come from recent ^{13}C-NMR measurements. In addition, only one single ^{139}La-NMR peak has supported the endohedral structure in which two La atoms are equivalently located in C_{80} cage [3].

Metal atom(s) rotation within a cage is expected to be a great help in designing functional molecular devices. It is a novel question whether encapsulated metal atom(s) are rigidly attached to cage carbons or move about. Recently, Akasaka et al. [90] have confirmed the circuit motion of two La^{3+} ions by observing the large broadening of the ^{139}La-NMR line-width due to the spin–rotation relaxation with increasing temperature. It is expected that such metal motion will lead to novel electronic and magnetic properties. This species might be used as an on–off switch to store and retrieve information in a small space.

3.3. Sc_2@C_{84}

For the C_{84} fullerene, there are 24 distinct isomers which obey the isolated pentagon rule [79]. The theoretical calculations show that three structures with D_{2d}, C_s and C_{2v} symmetry are close in energy and more stable for Sc_2@$C_{84.}$ This agrees with the fact that three isomers have been isolated and purified [91]. The STM study also showed that there were at least two different sizes in the image.

In the D_{2d} isomer, the two Sc atoms are equivalently encapsulated inside the C_{84} along the C_2 axis, bisecting the double bonds at the fusion of two hexagonal rings

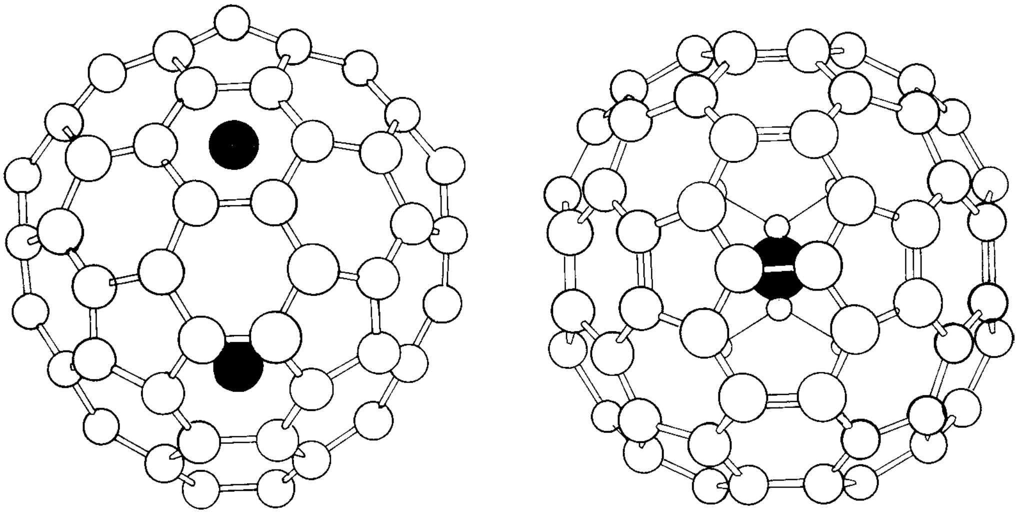

Fig. 5. Two views of the D_{2d} endohedral structure of $Sc_2@C_{84}$. In the D_{2d} isomer, the two Sc atoms equivalently encapsulated inside C_{84} along the C2 axis, bisecting the double bonds at the fusion of two hexagonal rings. Theoretical calculations show that the structure with D_{2d} symmetry is the most stable in energy for $Sc_2@C_{84}$.

(see Fig. 5). Yamamoto et al. [91] have succeeded in observing the ^{13}C-NMR lines (ten strong lines of nearly equal intensity and one line of half intensity) agree perfectly with the D_{2d} structure with 11 nonequivalent carbons. On the other hand, only one single ^{45}Sc-NMR signal observed confirms that the two Sc atoms are equivalent. Especially, Takata et al. [6] determined the endohedral nature of $Sc_2@C_{84}$ (isomer III) by a method that is a combination of the MEM and the Rietvel refinement from synchrotron powder diffraction data. The obtained MEM charge density clearly exhibits six- and five-membered rings and this configuration of the rings is exactly the same as that of the $C_{84}(D_{2d})$ cage. The two density maxima can be seen through the carbon cage and correspond to two Sc atoms, which indicates that $Sc_2@C_{84}$ is endohedral. The number of electrons around each maximum inside the cage is 18.8, which is very close to that of a divalent scandium ion Sc^{2+} (19.0). The MEM charge density of $Sc_2@C_{84}$ shows a strong contrast with that of $Y@C_{82}$ and $Sc@C_{82}$. The five- and six-membered ring networks of $Sc_2@C_{84}$ can be seen more clearly than those of $Y@C_{82}$ and $Sc@C_{82}$, which suggests that the rotation of $Sc_2@C_{84}$ molecules is virtually quenched in the solid even at room temperature (r.t.), whereas $Y@C_{82}$ and $Sc@C_{82}$ molecules might undergo hindered rotation. The Sc–Sc distance in C_{84} derived from the MEM charge density is 3.9 Å (4.029 Å theoretical value). The nearest Sc–C distance is 2.4 Å (2.35 Å theoretical value) [92].

Recently, the ^{13}C-NMR spectrum has been observed successfully for one of the other two isomers and exhibits a total of 46 lines [38 + 8 (half intensity)] [93]. This agrees with the C_s structure with 46 nonequivalent carbons. On the other hand, the ^{45}Sc-NMR spectra of this isomer show two distinct signals of equal intensity at 363 K and lower temperatures, indicating that two Sc ions in C_{84} are separated from each other and are located at inequivalent positions at this temperature range. At about 383 K, however, the two Sc ions move and rapidly exchange their positions, resulting in an equivalent NMR line [94]. Such a novel type of motion of metal atoms inside the fullerene cage could lead to a potential application of the metallofullerene as a ‘molecular device’ in future.

4. Electronic state and chemical property

The incorporation of metal atom(s) inside the fullerene results in an electron transfer from the metal atom(s) to the carbon cage under the formation of a stable ion pair. In this case, the endohedral metallofullerenes are particularly intriguing because the endohedral cations should have a highly charged anionic carbon cage for charge compensation. This should provide low-lying and delocalized charge-transfer states, which are important for large opticial nonlinearities and photoinduced reactions. For chemists, one of the most important things about these compounds is to understand the oxidation states of the metal atoms, which to a large extent determine the chemical behavior of the metallofullerenes. Theoretical calculations and some spectroscopy experiments have given abundant suggestions on electronic structures, oxidation states, and the amount of electron-transfer from the metal atom(s) to the fullerene cage.

Since the first preparation of metallofullerenes, great attention has been focused on the paramagnetic properties of these new materials to obtain information about the valence states of the metal ions and the charges on the fullerene cages. The first successful measurement of the EPR spectrum was achieved for La@C_{82} [95]. The observation of eight equally spaced lines provides remarkable confirmation of isotropic electron–nuclear hyperfine coupling (hfc) to ^{139}La, with nuclear spin quantum number 7/2; the *g* value is close to the free-spin value of 2.0023 (similar to those found for fullerene anion radicals), indicating that a single unpaired electron resides in the LUMO of the fullerene cage. Thus, it is suggested that the La($5d^16s^2$) atom donates its three valence electrons to the LUMO and the LUMO + 1 of C_{82} to form an endohedral complex with a $La^{3+}C_{82}^{3-}$ electronic structure. This is also supported from the observations of the UV photoelectron spectrum. Hino et al. [23] reported the first measurement of UV photoelectron spectra (UPS) for La@C82. The spectrum of La@C_{82} is analogous to those of C_{82}, but there is a distinct difference in the region just below the Fermi level: the presence of two new peaks at 0.9 and 1.6 eV with the intensity ratio of 1:2, which commences the transfer of three electrons from La to C_{82}. As in the case of La@C_{82} the EPR spectrum of Y@C_{82} consists of two strong lines, which arise from the $I = 1/2$ yttrium nuclei. The small value of the observed hyperfine coupling (0.48 G centered at $g = 2.00013$) indicates that the yttrium atom is in the 3 + oxidation state, resulting in the charge-transfer electronic state of $Y^{3+}C_{82}^{3-}$. In studies of Group-2-based samples (M = Ca, Sr, Ba), no EPR signals were observed [96], in contrast to EPR measurements of La@C_{82} and Y@C_{82}; the latter have a 3 + electronic state of the metal ion inside the cage and show EPR spectra due to an unpaired-spin electron at the carbon cage. For the former, it is suggested that almost two valence electrons on M (Ca, Sr, Ba) are transferred to be single paired in the LUMO of C_{82}. The resultant electronic structures are well described as $Ca^{2+}C_{82}^{2-}$, $Sr^{2+}C_{82}^{2-}$, $Ba^{2+}C_{82}^{2-}$. The closed-shell single ground states are consistent with EPR studies, which show no paramagnetic signal. In the study of Eu@C_{74} samples at r.t., no ESR spectra were observed. This supports the result of Raman measurements estimating a 2 + state of Eu ion inside the carbon cage [97].

As is well known, the EPR data cannot always be direct evidence for electronic structures of metallofullerenes. Although very small hyperfine coupling constants and near free-spin *g* values were observed for Sc@C_{82} [98], the Sc($3d^14s^2$) atom donates only its two 4s valence electrons to LUMO of C_{82}, leaving behind its 3d electron on Sc. Thus the electronic structure is formally described as $Sc^{2+}C_{82}^{2-}$. In addition, as a result of the transfer of two electrons from each Sc to C_{84} cage, Sc_2@C_{84} is also described as $(Sc^{2+})_2C_{84}^{4-}$. This is consistent with the electron-density distribution obtained from the powder diffraction data, as well as the X-ray photoemission spectroscopy [99]. It should be mentioned that Pr@C_{82} can be formally represented by Pr^{4+}@C_{84}^{4-} based on the experimental finding that Pr@C_{82} is EPR silent [100]. However, the UV–vis–NIR spectrum and X-ray photoemission spectroscopy (XPS) of Pr@C_{82} indicate that its electronic conformation is Pr^{3+}@C_{82}^{3-}.

The UV–vis–NIR absorption spectrum of Pr@C_{82} resembles those of La@C_{82}, Y@C_{82}, Gd@C_{82}, Nd@C_{82}, Tb@C_{82}, Lu@C_{82} and Ce@C_{82} [101–103]. Incorporation of a single trivalent ion in C_{82} induces a broad absorption band peaking at 1400 nm and extending down to 2300 nm; this absorption feature is attributed to their open-shell electronic structures. The UV–vis–NIR absorption spectra of La_2@C_{80}, Pr_2@C_{80} and Ce_2@C_{80} are very similar, exhibiting a monotonically decreasing function of wavelength without any sharp absorption features [104]. C_{80} in M_2@C_{80} (M = La, Pr, Ce) acquires the six valence electrons from the two M atoms, presumably forming the same electronic structures $(M^{3+})_2C_{80}^{6-}$. The closed-shell electronic structure of C_{80}^{6-} in M_2@C_{80} is likely to account for the absence of NIR absorption peaks in the spectrum. Recently, Wang et al. [105] reported that very few similarities on their absorption features were seen for the two isomers of Sc_2@C_{82} as well as for the two isomers of Sc_2@C_{86}. A previous investigation on Sc_2@C_{84}(I–III) also revealed that the absorption spectra for the three isomers are very different from each other [106]. This indicates that the electronic structures of discandium metallofullerenes should be dominated by the fullerene cages rather than the endohedral metal atoms.

The XPS of deep core levels provides a direct measure of the valency of each atom in the compound and has been proved to be a suitable probe of the chemical state of La in La@C_{82}. In this case, the position and the shape of the La 3d XPS peak of La@C_{82} are rather similar to those of various La trihalides, suggesting that the oxidation state of La is + 3. In studies for Ce@C_{82} and Ce_2@C_{80}, similar results were also obtained. However, the XPS measurement of Tm@C_{82} confirms that this material is a monometallofullerene containing a divalent Tm^{2+} ion. The position of the Tm 4d main line in the XPS spectrum is shifted by about 2.5 eV to lower BE in comparison to that in the trivalent Tm metal (175.2 eV BE) [107]. The Sc 2p XPS core level of Sc_2@C_{84} was found to be located just between those of the metal and the oxide (Sc_2O_3). This suggests that Sc atoms encapsulated in C_{84} take an intermediate valence between those of the metal (Sc^{0+-}) and oxide (Sc^{3+}).

Because only small amounts of the materials are available, electrochemistry is a quite useful method for characterizing metallofullerenes, especially the EPR-silent ones. Suzuki et al. [108] reported the first voltammograms of the pure La@C_{82}, which exhibits five reversible reduction and one reversible oxidation processes. Lately, the results of the voltammograms of the pure fullerenolanthanides, $La@C_{82}$, $Y@C_{82}$, $Ce@C_{82}$ and $Gd@C_{82}$ were also obtained [103]. It is indicated that these fullerenolanthanides are stronger electron donors as well as stronger electron acceptors than empty fullerenes. The first oxidation potential of $La_2@C_{80}$ is much more anodic than those of $La@C_{82}$, suggesting that $La_2@C_{80}$ is a weaker electron donor than the $La@C_{82.}$ The first reduction potential of $La_2@C_{80}$ is anodically shifted relative to those of $La@C_{82}$, implying that $La_2@C_{80}$ is a stronger electron acceptor than the $La@C_{82}$ [109].

It is generally accepted that three-electron transfer is favorable when M = Y, La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, Lu, but Sc, Eu, Sm, Yb, Tm, Ca, Sr, Ba prefer to donate two electrons to the fullerene cages.

The calculations show that the electrostatic potential inside the carbon cage is positive at any position [110]. However, this situation is drastically changed as electrons are transferred to the carbon cage from the metal atom. The electrostatic potentials become highly negative. The inside of the negatively charged cage is very suitable for accommodating cations, which is the reason why encapsulated metals prefer to take highly cationic.

Ionization potentials (Ip) and electron affinities (Ea) play an important role in characterizing electronic properties which are expected to determine the chemical behavior of endohedral metallofullerenes to a certain extent. The calculations by Nagase and Kobayashi [111] showed that the Ip values for $M@C_{82}$ are 1.2–1.6 eV lower than those for C_{60} and C_{70}, whereas the Ea values for $M@C_{82}$ are 0.4–0.7 eV higher than those for C_{60} and $C_{70.}$ This is consistent with the shift of the first oxidation and reduction potential peaks measured for $Y@C_{82}$ and $La@C_{82}$, relative to those of C_{60} and C_{70}, which indicates that endohedral metallofullerenes act as a stronger electron donor as well as a stronger electron acceptor.

A large number of experimental studies have been performed on the chemical derivatization of empty fullerenes such as C_{60} and $C_{70.}$ Up to now, however, the chemical properties of endohedral metallofullerenes have been studied scantily due to the low yield and separation difficulties. It is of great interest whether endohedral metallofullerenes can also be functionated and how the reactivities of empty fullerenes are modified by the endohedral doping of metal atom(s).

Akasaka et al. [112–114] published the first chemical derivatization of isolated $La@C_{82}$, $Gd@C_{82}$ and $La_2@C_{80}$ by disilacyclopropane. It was found that the three endohedral metallofullerenes can be derived by the photochemical reactions and lead to the formation of a cycloadduct, as in the cases of empty fullerenes. It has been known that the higher fullerenes (C_{76}, C_{78}, C_{82} and C_{84}) as well as C_{60} and C_{70} do not react thermally with disilacyclopropane. A remarkable finding is that the three metallofullerenes react thermally with disilacyclopropane to provide 1:1 adducts. This is due to their lower reduction potentials than those of empty fullerenes. On the other hand, the thermal addition of disilacyclopropane to $Sc_2@C_{84}$ (D_{2d}) is suppressed, as in empty fullerenes, because of the higher reduction potential of $Sc_2@C_{84.}$ These results suggest that the thermal additions are initiated by electron transfer from disilacyclopropane to endohedral metallofullerenes with strong electron-accepting character as well as the reactivity of empty fullerenes being highly controlled by endohedral metal doping. Since the electronegativities of germanium and silicon are similar, it is also found [115] that photochemical and thermal reactions of $La@C_{82}$ with digermacyclopropane afford an exdohedral adduct (1:1). Even when the reaction temperature decreased by 20°C, the thermal addition digermacyclopropane onto $La@C_{82}$ was observed, unlike the disilacyclopropane case (the reaction temperature 80°C). This is accounted for by the fact that digermacyclopropane has a lower oxidation potential than disilacyclopropane.

Paramagnetism of $La@C_{82}$ and $Y@C_{82}$ allows one to selectively investigate the reactivity of these compounds, with small amount in hands admixed to empty fullerenes by EPR spectroscopy. Recently, Tumanskii et al. [116–118] studied the reactivity of $La@C_{82}$ in a mixture with C_{60} and C_{70} versus L_2Pt°, phosphoryl radical $^{\bullet}P(O)(OR)_2$, and CF_3COOH using EPR spectroscopy. The two former reagents did not change the EPR spectrum, whereas when an excess of CF_3COOH was added to a toluene solution of the same mixture containing $La@C_{82}$, signals of isomers 2 disappeared and new signals appeared. They can be assigned to protonated species $[M@C_{82}H]^{+\bullet}(OCOCF_3)^-$. Multiplets of isomers 1 did not change. Similar behavior was also found upon treatment of $Y@C_{82}$ with CF_3COOH. It is indicated that endohedral metallofullerenes $La@C_{82}$ and $Y@C_{82}$ can be protonated by CF_3COOH in accordance with the nucleophilic character of the carbon cage and the acid can distinguish two isomers. The chemical reactions of $La@C_{82}$ and diphenyldiazomethane (Ph_2CN_2) have been reported and the products (several possible isomers) have been characterized by EPR [119].

Recently, we synthesized two new exdohedral adducts of endohedral metallofullerenes — water soluble multihydroxyl endohedral metallofullerols ($Gd@C_{82}(OH)_m$ $m = 20$ and $Pr@C_{82}O_m(OH)_n$ $m = 10$, $n = 10$) [120,121]. Water-soluble endohedral metallofullerene derivatives are very important and may have application in the field of biomedicine. The successful derivatization of endohedral metallofullerenes would inspire much more work on the chemical properties.

5. Mass spectrometry study

Originally, due to the scarcity of metallofullerenes and the fact that the species were always found in mixtures with empty fullerenes, sensitive analytical techniques such as MS, EPR and XPS were used to study the endohedral metallofullerenes. Mass spectrometry, especially, provided the crucial evidence that led to the discovery of metallofullerenes in 1985 [122], and has always played a key role in the identification and characterization of metallofullerenes [123]. This role has been much greater in recent years through the applications of developed techniques, such as 'soft' ionizations, collisional dissociation, tandem MS techniques, etc.

Metallofullerenes were first observed in laser vaporization MS experiments. Using a laser-vaporized graphite disk impregnated with lanthanum, under surroundings of helium buffer gas, Heath et al. [122] found C_{60}^+, C_{70}^+, and LaC_n^+ clusters in the time-of-flight mass spectrum. The high photophysical stability of LaC_n^+ led to the postulation that the metal was inside the cage. Confirmation of its endohedral nature was obtained with a cluster beam/Fourier transfer ion cyclotron resonance (FT/ICR) mass spectrometer by nonreactions with O_2, NO, and NH_3 but with laser irradiation producing C_2 loss from the LaC_{60}^+ until LaC_{44}^+, showing that the carbon cage bursts at a point dictated by the ionic radius of the internal atom [124]. Later 'shrink wrapping' experiments showed that the smallest cage that can surround two lanthanum atoms is C_{66}, and the minimum cage that can fit around three is $C_{88.}$ On the other hand, the experiments [125] verified that externally attached metal atoms do so in a radically different way; they react readily and are easily knocked off.

Laser desorption/ionization time-of-flight mass spectrometry is a newly developed mass spectrometry technique. Using an impulsing laser to desorb samples, it has become an excellent analytical tool due to its advantages of rapidity, high sensitivity, and lesser amounts of samples to be used. In most cases, positive-ion LD–TOF mass spectra are usually collected for other samples. However, the situation is different for the analysis of the endohedral metallofullerenes: under similar analytical conditions, the negative-ion mass spectrum is much better than the positive-ion mass spectrum when the resolution, sensitivity and S/N ratio.

Dunsch et al. [126] reported that in terms of a sector field mass spectrometer was applied to analyze and generate fullerene and metallofullerene ions with different ionization methods, the results showed that NCI (negative ion chemical ionization) is the best ionization method in comparison with PCI, MEI, and FAB (PFAB, NFAB). The sensitivity of the detection by NCI is a thousand times higher than that of other ionization methods.

It should be pointed out that LDI–TOF MS can determine the components in metallofullerene extracting solutions (mixtures of fullerenes and metallofullerenes) qualitatively but not quantitatively. The absorptivities of empty fullerenes and metallofullerenes to laser are different; this will lead to the mass discrimination of the components that absorb laser strongly. For example, empty fullerenes, with an Ip of about 7.6 eV for C_{60}, require two 193 nm (6.4 eV) photos for ionization. The Ip of $La@C_{2n}$ are between $6.2 \sim 6.4$ eV and require only one 193 nm photo for ionization. The difference between the linear one-photo and quadratic two-photo ionization processes results in a strong enhancement of the metallofullerene signal [127]. However, this mass discrimination is similar for all metallofullerenes and does not influence the determination of the relative yield of metallofullerenes on the basis of peak intensity.

Mirroring studies in condensed-phase mass spectrometry provide a powerful tool for chemical property research. In our previous studies [128–130], the gas-phase ion/molecule reaction of C_{60} with ions derived from small organic compounds has been investigated. The results showed C_{60} possessing the twofold reactivities of 'superalkenity' and 'superaromaticity'. Authors also reported [131–133] gas-phase ion–molecular reactions of endohedral metallofullerenes with the self-CIMS ion systems of vinyl acetate, benzene and acetone in the ion source of the mass spectrometer; several derivatized endohedral metallofullerene cations $[M@C_{82}–C_2H_3O]^+$, $[M_2@C_{80}–C_2H_3O]^+$, $[M@C_{82}–C_6H_6]^+$, and $[M@C_{82}–CO–CH_3]^+$ were observed as the major products. The results indicate that endohedral metallofullerenes are fairly reactive and might undergo varieties of gas-phase reaction routes, such as $[2+3]$ cycloaddition, π–π interaction and δ-addition reactions, and so on.

Ion mobility measurements are the most direct method for analysis of carbon clusters in the gas phase to obtain the information of structures and formation mechanism of endohedral metallofullerenes. The method is based on the fact that the mobility of a cluster ion in a buffer gas depends on its shape. The ion clusters travel across the drift tube under the influence of a weak electric field, and the drift time depends on the geometry of the cluster. Clusters with compact geometries have shorter drift time than clusters with less compact geometries. The resulting drift-time distribution provides information about the structures and their relative abundances. Ion mobility measurements of gas-phase LaC_n^+ ions indicate that the atom La is always endohedral unless the carbon cage is too small to accommodate the metal atoms [134–137]. On the other hand, $La_2C_n^+$ always exists as a mixture of $La@C_nLa^+$ and $La_2@C_n^+$ even though the carbon cages were large enough to easily encapsulate the two lanthanum atoms [138]. Clemmer et al. [136] reported that laser vaporization of a La_2O_3/graphite rod produced a number of LaC_{60}^+ isomers in which lanthanum seems to be bound to polycyclic polyyne rings. Upon annealing it was found that nearly all the different ring isomers converted spontaneously into endohedral metallofullerenes with remarkably high efficiency (> 98%). It was suggested that in the first step of the annealing process the lanthanum atom acts as a nucleation center and the carbon rings arrange themselves around the lanthanum atom before converting into a fullerene cage.

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