

Another Big Discovery – Metallofullerenes –

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Summary

Several days after the first experimental observation of the ‘magic number’ soccerball-shaped C_{60} in a laser-vaporized cluster beam mass spectrum by Kroto, Smalley and coworkers, they also found a magic number feature due to $La@C_{60}$ in a mass spectrum prepared by laser vaporization of a $LaCl_3$ impregnated graphite rod. With the advent of macroscopic synthesis and the following successful separation and purification of metallofullerenes, both experimental and theoretical studies of metallofullerenes have developed quite rapidly to date so as to elucidate their structural, electronic, magnetic and transport properties. Furthermore, a bottom-up closed network growth mechanism has experimentally been shown to play a crucial role in forming various types of metallofullerenes.

Retrospect

I still saw a stack of reprints (with color covers) of the famous C_{60} Nature paper on a desk in Harry Kroto’s office when I first visited him in Sussex. It was June 1986, a half year later of the publication. I vividly remember the day when he said to me “Nori (my nickname), why don’t you take some of these reprints and distribute them to your research friends in Japan.” I received 5-6 reprints from him. Exactly 30 years have passed since then, and, in fact (thanks to this event), my research topic made a big (and fortunate) transition from gas-phase supersonic microcluster beam studies to carbon nanomaterials including fullerenes and endohedral metallofullerenes, fullerenes with metal atom(s) encapsulated. Unfortunately, I missed forever a chance to acknowledge this to Harry even though we have been collaborating on the growth mechanism of metallofullerenes during the past decade. Fortunately, however, as a memory of this happy event, I still have one of the Nature reprints he handed me. I would like to dedicate this article to Harry Kroto.

Experimental Evidence

Kroto, Smalley and coworkers found a magic number feature due to LaC_{60} in a mass spectrum prepared by laser vaporization of a $LaCl_3$ impregnated graphite rod [1] several days after the discovery of C_{60} . They observed a series of C_n^+ and LaC_n^+ ion species with LaC_{60}^+ as a magic number ion in the mass spectrum (Figure 1) and concluded that a La atom was encaged within the (then

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hypothetical) soccerball-shaped C_{60} . This was obviously the first proposal of the so-called 'endohedral metallofullerene' based on experiments. They first tried Fe with no success and found that La is a correct atom for encapsulation within fullerenes. It is interesting to note that even today Fe has not been encapsulated by fullerenes. I think that this Kroto and coworkers' study (experimentally showing the presence of "metallofullerenes") was or is another big discovery and breakthrough in carbon nanomaterials science.

The first production of macroscopic quantities of endohedral metallofullerenes were reported by Smalley and coworkers [2]. They used high-temperature laser vaporization of La_2O_3 /graphite composite rods to produce various sizes of La-containing metallofullerenes. Contrary to the previous expectation, only the $La@C_{82}$ fullerene was extracted by toluene solvent even though $La@C_{60}$ and $La@C_{70}$ were also seen in the mass spectra of the sublimed film from soot. In other words, the major La-metallofulleren with air and solvent stability is $La@C_{82}$, and $La@C_{60}$ and $La@C_{70}$ are somehow unstable in air and solvents.

In January 1991 during hectic years of the beginning of fullerene research, my research team decided to narrow down our own research target to metallofullerenes. Our first report was beaten out by Smalley's group at Rice University, but our metallofullerene research went very well. In 1995, we were able to obtain the first experimental proof of the encapsulation of metal atoms through synchrotron X-ray diffraction [3]. Interestingly, the instant the metal atom entered the fullerene, two or three of the outer electrons of the metal atom transferred to the fullerene cage. This phenomenon is called intra-fullerene electron transfer, and we found that we could create fullerenes with very interesting electronic and electron transport properties that could not be obtained with normal empty fullerenes. In the early stages of metallofullerene research, fullerenes encapsulating group 3 (Sc, Y, La) or lanthanide elements (Ce through Lu) were produced, but it is now possible to encapsulate similarly group 2 (Ca, Ba, Sr) and group 4 (Ti, Zr, Hf) atoms inside fullerenes.

The important event during the early stage of growth is whether or not the metal atom enters the fullerene and is present inside until the opening of the fullerene closes. Electron transfer occurs from the metal to the fullerene, and it is preferable to have a metal atom where a strong coulombic attraction operates. However, transition metals, such as iron, cobalt and nickel, do not give rise to efficient electron transfer with the fullerene. Therefore, the metal atom detaches from the fullerene during production at high temperatures. In this case, no metallofullerene is produced.

Interestingly, it later became clear that metal atoms, such as iron, cobalt, and nickel, where electron transfer virtually does not occur, are important metal catalysts for single-wall carbon nanotube synthesis. However, the metals that will go into fullerenes do not make efficient nanotube catalysts. Metallofullerenes and carbon nanotubes are materials that are very similar to each other, and we can assume that there is a fine line between one becoming a metallofullerene or a nanotube during the initial stages of production.

Synthesis, Separation and Purification

Metallofullerenes can be synthesized typically in two ways similar to the synthesis of the normal empty fullerenes, which involves the generation of a carbon-rich vapor or plasma in He or Ar gas atmosphere. The two methods have been routinely used to date for preparing macroscopic amounts of

metallofullerenes: the high-temperature laser vaporization or the ‘laser-furnace’ method and the DC arc discharge method. Both methods simultaneously generate a mixture of hollow fullerenes ($C_{60}, C_{70}, C_{76}, C_{78}, C_{84}, \dots$) together with metallofullerenes. The production of metallofullerenes can be followed by procedures to extract from soot and to separate/purify the metallofullerenes from the hollow fullerenes.

Figure 2 represents a third-generation large-scale DC arc discharge apparatus for the production of metallofullerenes developed and installed at Nagoya University [4]. The arc generator consists of a production chamber and a collection chamber, equipped with an anaerobic sampling and collection mechanism of raw soot containing metallofullerenes. Anaerobic sampling of the soot is preferred to conventional collection under ambient conditions because many of the metallofullerenes in primary soot are air (moisture)-sensitive and may be subjected to degradation during the soot handling. Metal-oxide/graphite composite rods, e.g. La_2O_3 to prepare $La@C_{82}$, are normally used as positive electrodes (anodes) after a high-temperature (above ca $1600^\circ C$) heat treatment where the composite rods are cured and carbonized. At such high temperatures, various metal carbides in the phase of MC_2 are formed in the composite rods, which actually is crucial to an efficient production of endohedral metallofullerenes: uniformly dispersed metal atoms as metal-carbides in a composite rod provide metallofullerenes in higher yields. In general, the yield of a metallofullerene varies sensitively on He buffer gas pressure during the arc synthesis. An optimum He pressure depends on arc conditions such as the size of a composite rod, DC current, and the arc gap of the two electrodes, which is normally close to that of empty higher fullerenes such as C_{82} and C_{84} .

As in the case of hollow fullerenes, liquid chromatography (LC) is the main purification technique for metallofullerenes. LC has been frequently and traditionally used in separation chemistry. One of the most powerful LC techniques is the so-called high-performance LC (HPLC) which allows separation of fullerenes according to their molecular weight, size, shape or other parameters. The HPLC technique can even allow us to separate structural isomers of various metallofullerenes [4]. The purification of endohedral metallofullerenes via HPLC had been difficult, mainly because the content of metallofullerenes in raw soot is normally very limited and, furthermore, the solubility in normal HPLC solvents is generally lower than that of various empty higher fullerenes. It took almost two years for metallofullerenes to be completely isolated by the HPLC method [5,6] after the first extraction of $La@C_{82}$ by the Rice group [2]. The success of the purification/isolation was a real breakthrough for further and detailed characterization of the endohedral metallofullerenes.

X-ray Structural Analyses

Since the first studies on production and solvent extraction of metallofullerenes such as $La/Y/Sc@C_{82}$, there had been great controversy as to whether or not the metal atom is really trapped inside the fullerene cage. The first conclusive experimental evidence on the endohedral nature of a metallofullerene, $Y@C_{82}$, was obtained by a synchrotron X-ray diffraction study [3]. The result indicated that the yttrium atom is encapsulated within the C_{82} fullerene and is strongly bound to the carbon cage [3]. The MEM (maximum entropy method) electron density distribution of $Y@C_{82}$ is shown in Figure 3. There exists a high-density area just inside the C_{82} cage. The density maximum at the interior of the C_{82} cage corresponds to the yttrium atom, unequivocally indicating the endohedral structure of the metallofullerene.

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The MEM election density map further reveals that the yttrium atom does not reside at the center of the C₈₂ cage but is very close to the carbon cage as suggested theoretically [7,8]. The studies suggested the presence of a strong charge transfer interaction between the Y³⁺ ion and the C³⁻ cage which may cause the aspherical electron density distribution of atoms. The X-ray study also reveals that the Y@C₈₂ molecules are aligned along the [001] direction in a head-to-tail (...Y@C₈₂ ...Y@C₈₂ ...Y@C₈₂ ...) order in the toluene (as a solvent) containing crystal, suggesting the presence of a strong dipole–dipole and charge transfer interactions among the Y@C₈₂ fullerenes.

On account of the inherent spherical shape of fullerenes, it had been difficult to obtain high quality single crystals [4]. However, the random rotation of the spherical fullerene cage can be suppressed by chemical modification or co-crystallization with suitable compounds. One of the frequently used and common techniques to obtain single crystals of metallofullerenes is to employ co-crystallization with metal porphyrin compounds, which was originally developed by Balch, Dorn and coworkers [9]. The technique has extensively been applied to single crystal X-ray structural determination of metal nitride metallofullerenes of the type M₃NC₈₀ (M=metals) in particular. The co-crystallization procedure produces samples with sufficient order due to the non-covalent interactions between the metal porphyrin and the fullerene cage.

Metal-Carbide Metallofullerenes: A Quantum Gyroscope

The production and isolation of the first carbide metallofullerene was reported on Sc₂@C₈₆ (=Sc₂C₂@C₈₄) in 2001 [10]. Very interestingly, this carbide metallofullerene was an accidental discovery when Wang et al. were trying to isolate and spectroscopically characterize Sc₂@C₈₆ (=Sc₂C₂@C₈₄) and Sc₂@C₈₈ (=Sc₂C₂@C₈₆) [11]. Up until these studies, none had come up with the idea that Sc₂@C₈₆ is actually a carbide Sc₂C₂@C₈₄ metallofullerene, because the normal identification technique for metallofullerenes is mass spectrometry in which only mass numbers can be identified. In the ensuing years, it had been revealed that the major part of the di-scandium metallofullerenes may have Sc₂C₂@C_{2n-2} carbide structure rather than pure scandium Sc₂@C_{2n} metallofullerenes including Sc₂@C₈₄ (isomers III) [12,13]. The schematic molecular structure of Sc₂C₂@C₈₄ is shown in Figure 4. It was found that the C₂ molecule in the C₈₄ cage is rotating like a rigid-rotor at low temperatures below 60 K as described followings [14].

Kuzmany and coworkers observed the quantized rotational states of a diatomic C₂ unit in solid a scandium carbide metallofullerene Sc₂C₂@C₈₄ [14]. They found that the rotational transitions of C₂ unit in the C₈₄ fullerene cage induce a well-resolved periodic line pattern in the low energy Raman spectrum. The rotational constant *B* and the C-C distance were found to be 1.73 cm⁻¹ and 0.127 nm, respectively. Density functional calculations revealed an intrinsic rotational barrier of the order of only a few meV for the C₂ unit. The Schrödinger equation involving the potential barrier was solved and the Raman tensor matrix elements were calculated, which provides perfect agreement with the experiment. This carbide metallofullerene can present the first intrinsic rotational spectrum of a diatomic plane molecular rotor, a “quantum gyroscope”. Michel et al. reported a rigorous study of the superposition of the quantum rotational motion of C₂ unit and classical rotation motions of the surrounding C₈₄ carbon cage in Sc₂C₂@C₈₄ [15]. Figure 5 presents a dynamic molecular structure obtained from molecular dynamics calculations. These

calculations provide a first indication that $C_2@Sc_2C_{84}$ is a more realistic formula than $Sc_2C_2@C_{84}$ for this carbide metallofullerene. Comprehensive treatments on the carbide metallofullerenes can be found in a recent review article [16].

Non-IPR Metallofullerenes

IPR (isolated pentagon rule) can be considered as THE most important and essential rule governing the geometry of fullerenes. As Harry Kroto first proposed [17], IPR simply states that the most stable fullerenes are those in which all pentagons are surrounded by five hexagons. All the empty fullerenes so far produced, isolated and structurally characterized to date have been known to satisfy IPR. IPR can be best understood as a logical consequence of minimizing the number of dangling bonds and steric strain of fullerenes [18]. As a result, the smallest IPR-satisfying fullerene is C_{60} , and C_{70} is the second smallest; there are no IPR fullerenes between C_{60} and C_{70} .

Although IPR, in principle, has been equally applied for metallofullerenes, IPR isomers of a metallofullerene can be different from those of the corresponding empty fullerene. In metallofullerenes, electron transfers from an encaged metal atom to the carbon cage may drastically alter the stability and electronic structure of the fullerene. Shinohara and coworkers [19] and Dorn and coworkers [20] independently synthesized and structurally characterized IPR-violating (non-IPR) metallofullerenes, $Sc_2@C_{66}$ (Figure 6) and $Sc_3N@C_{68}$, respectively. Interestingly, $Sc_2@C_{66}$ has two fused-pentagon and $Sc_3N@C_{68}$ has three fused-pentagon on the fullerene cage.

Since these reports, many non-IPR metallofullerenes have been produced, isolated and structurally characterized. Even a non-IPR carbide metallofullerene, $Sc_2C_2@C_{68}$, was isolated and structurally characterized [21]. The violation of IPR in endohedral metallofullerenes can generally be explained by the changes of the relative stability of the metallofullerenes with the increase of the negative cage charge. One of the probable theoretical rationales for the stability of non-IPR metallofullerenes is presented by Slanina, Nagase and coworkers [22]. Although a fused-two-pentagon is an 8π anti-aromatic system in its neutral state, it becomes 10π aromatic system in the 2- anionic state [23]. In non-IPR metallofullerenes, when the encapsulated metal atom in the metallofullerenes donates two electrons to the pentagon pair, the fused pentagon moiety becomes aromatic.

A general tendency of the fullerene cage size dependence on the appearance of fused-pentagons is that the number of fused-pentagon decreases as the cage size increases. In larger fullerene cages, pentagons should tend to be distributed over the entire fullerene cage and the presence of fused-pentagons, which cause both steric strain and electronic charge density localization, becomes more and more energetically unfavorable. In contrast, in smaller cages normally than C_{80} aside from several exceptions, the appearance of fused-pentagons becomes statistically more frequent.

The experimental discovery of the non-IPR metallofullerenes indeed let one recognize the unexpected further diversity of the fullerene pentagon-hexagon geometry. The current state-of-the-art studies of non-IPR metallofullerenes is well reviewed and summarized by Xie and coworkers [24].

Growth Mechanism

One of the biggest mysteries in metallofullerene science is its growth mechanism: how a metallofullerene could evolve and form from high-temperature carbon vapor/plasma. It is extremely important to know how fullerenes/metallofullerenes are formed in high temperature plasma of arc-discharge or laser vaporization, because the elucidation of the growth mechanism may lead to high yield syntheses/fabrications of the metallofullerenes. Unfortunately, so far experimental techniques to probe growth processes of fullerenes are very limited due to the very high temperature (4,000 – 10,000 C) reactions inherently involved. Moreover, it is still not known whether or not the growth of the metallofullerenes is similar to that of empty fullerenes because of the presence of metal atoms (which definitely play some “catalytic” roles for the formation).

Because of the inherent difficulty to directly probe the growth process of macroscopically obtainable metallofullerenes such as $M@C_{82}$ (M =metal atom), even today, detailed experimental investigations on the formation mechanism have so far been very limited. One of the main reasons of this is that the formation of metallofullerenes is basically occurring under plasma conditions at very high temperatures like 4,000-10,000 K either by laser-ablation or arc-discharge synthesis. However, it has been known that there are two primary important routes for growth of endohedral metallofullerenes: (1) top-down formation, i.e., a graphite fragment originating from the target is directly involved; (2) bottom-up growth, i.e., formed initially from small carbon clusters and atomic carbon. In the following, both mechanisms are discussed based on the recent experimental studies.

One of the serious drawbacks of the to-down mechanisms is that the presence of giant fullerenes has not been experimentally confirmed. The top-down mechanisms are based on the fact that very-large fullerenes, the so-called giant fullerenes, exist in carbon plasma. The only experimental evidence they ascribed are mass spectral observation of row soot containing fullerenes/metallofullerenes, where the fullerenes as large as C_{200} or larger can be seen. In a sense, this is true but very misleading. It is important to recognize that mass spectra of fullerenes/metallofullerenes have led oftentimes to misunderstanding in discussing the amount of fullerenes, particularly that of higher fullerenes.

Dunk, Kroto and coworkers reported direct experimental evidence for a bottom-up growth of metallofullerenes [25] (Figure 7). Figure 8 shows fullerene cage behaviour and reactivity of $Pr@C_{82}$ in the presence of high-temperature carbon vapor evaporated from graphite and in a low-pressure of buffer He gas. $Pr@C_{82}$ is shown to undergo C_2 insertion reactions to form $Pr@C_{84}$ in high abundance. Interestingly, an inverse reaction by C_2 -loss to $Pr@C_{80}$ essentially does not occur. As shown in Figure 8, extensive C_2 insertion reactions form metallofullerenes significantly larger than $Pr@C_{84}$, including very large metallofullerenes ($> M@C_{100}$). The smaller fullerenes observed than $Pr@C_{82}$ are primarily empty ones which result from bottom-up growth of C_{80} together with low abundance $Pr@C_{80}$ and $Pr@C_{78}$. The fullerenes C_{80} , $Pr@C_{78}$ and $Pr@C_{80}$ can be attributed to result from an unavoidable laser fragmentation of the vaporization laser and the $Pr@C_{82}$ starting material. Importantly, smaller $M@C_{2n}$ ($2n < 76$) metallofullerenes, although abundantly generated by vaporization of graphite, are entirely absent in the figure. They also reported similar bottom-up formation of medium-sized fullerenes to larger metallofullerenes with other metal atoms encapsulated in $M@C_{82}$ such as $Y@C_{82}$ and $Yb@C_{82}$.

The bottom-up metallofullerene formation mechanism that Dunk, Kroto and coworkers proposed [25-27] seems to well explain many experimental observations, including the long-standing issue of

“isotope scrambling experiments” previously described [28,29]. Those studies establish that amorphous ^{13}C is statistically incorporated into fullerene cages when combined with graphite and subsequently evaporated by means of the arc discharge or laser ablation synthesis method. This strongly indicates that graphite is initially transformed into small carbon species such as C and C_2 , which then react to ultimately generate metallofullerenes. In fact, that process has so far been demonstrated repeatedly during the past couple of decades considering the large number of reports which utilize formation of ^{13}C -enriched metallofullerenes for ^{13}C NMR spectroscopic study [16]. The bottom-up growth mechanism seems much likely because of the direct experimental observation of C_2 -incorporation (digestion) into fullerenes/metallofullerenes to form larger fullerenes. Further studies are needed, however, as to whether or not the bottom-up growth is equally valid in arc-discharge and combustion synthetic conditions as in laser-ablation described here.

Acknowledgement

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Competing Interests

I have no competing interests.

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Figures

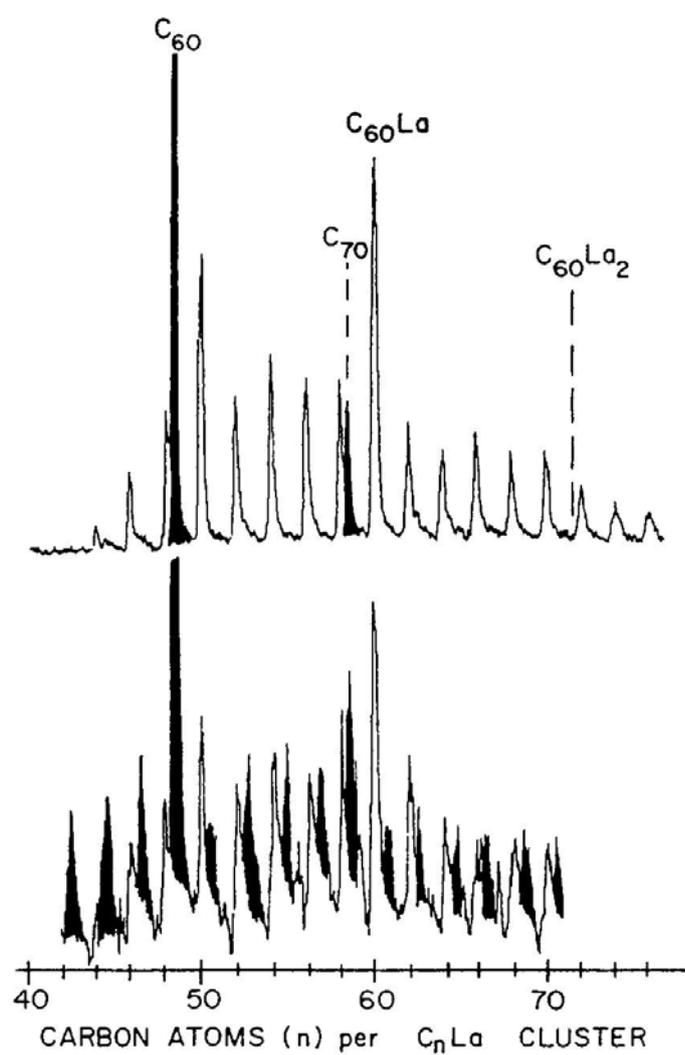
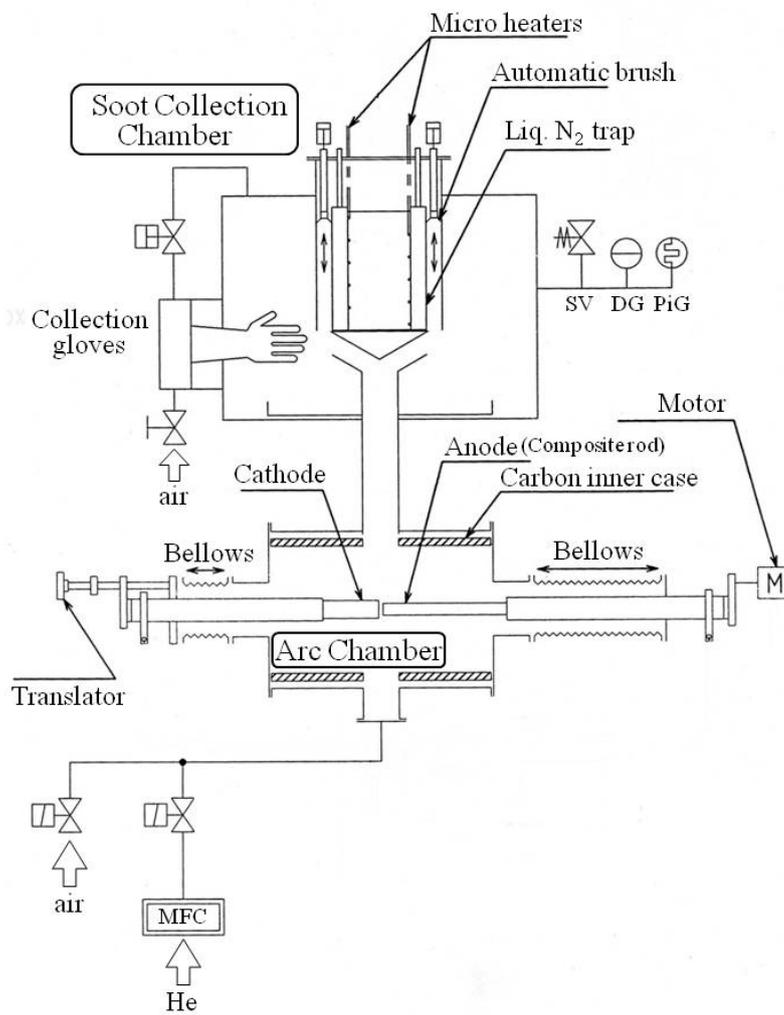


Fig.1

**Fig.2**

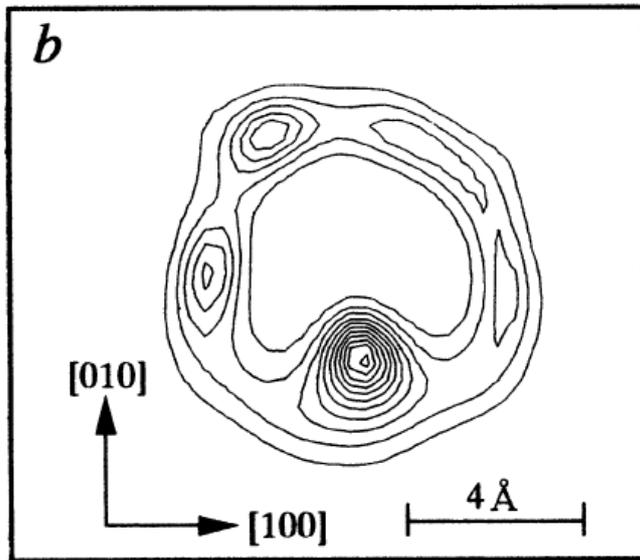


Fig. 3

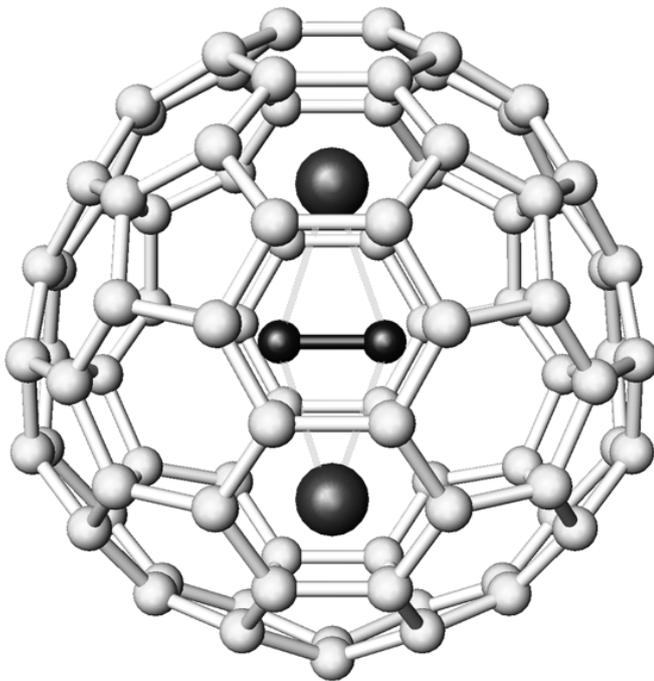


Fig. 4

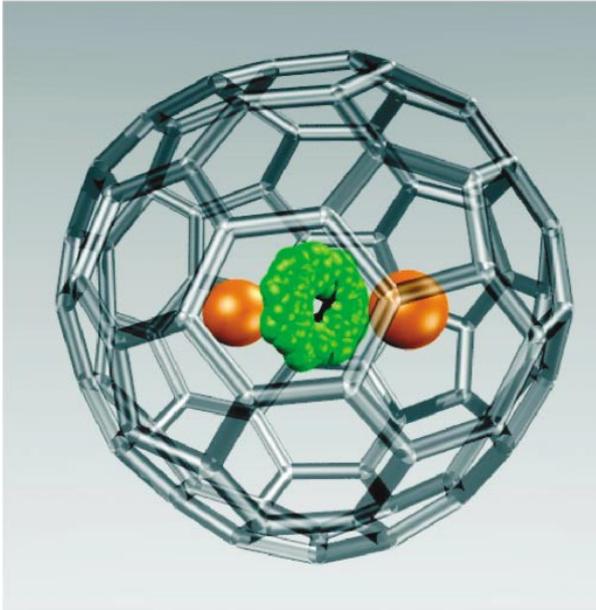


Fig.5

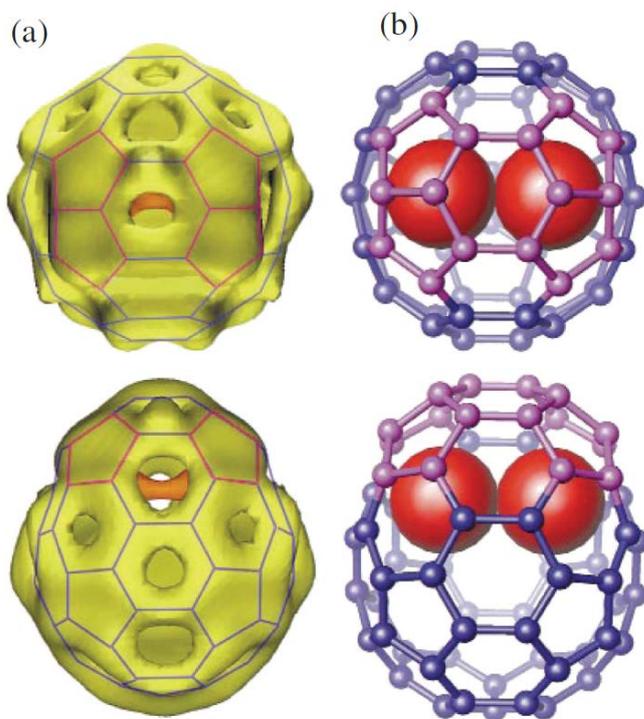
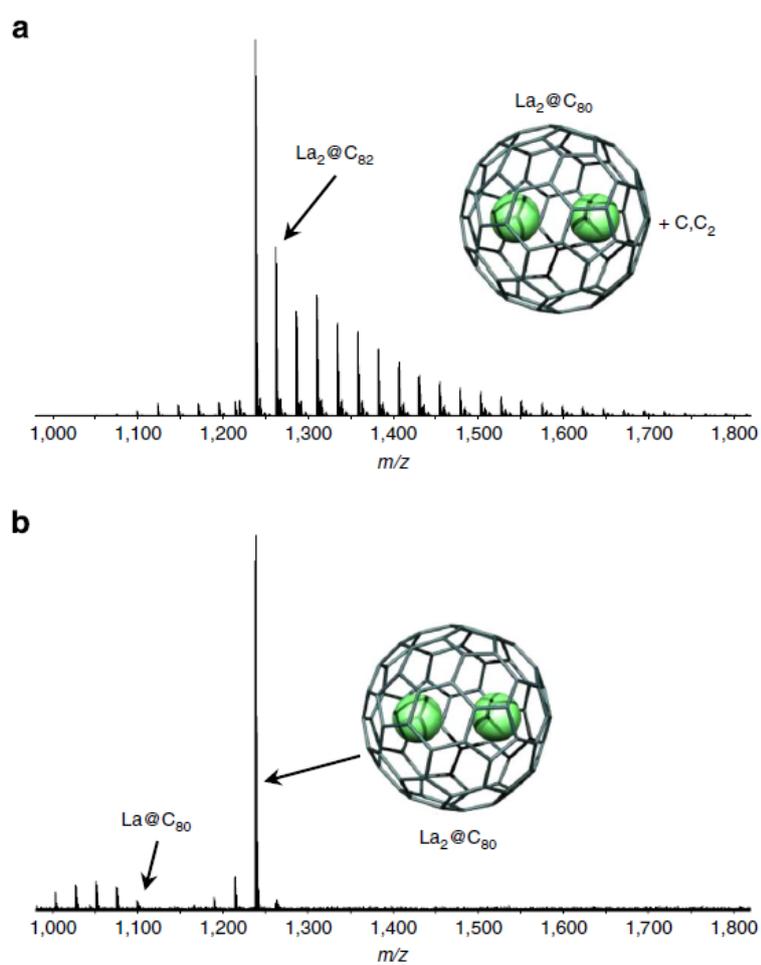


Fig.6

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**Fig.7**

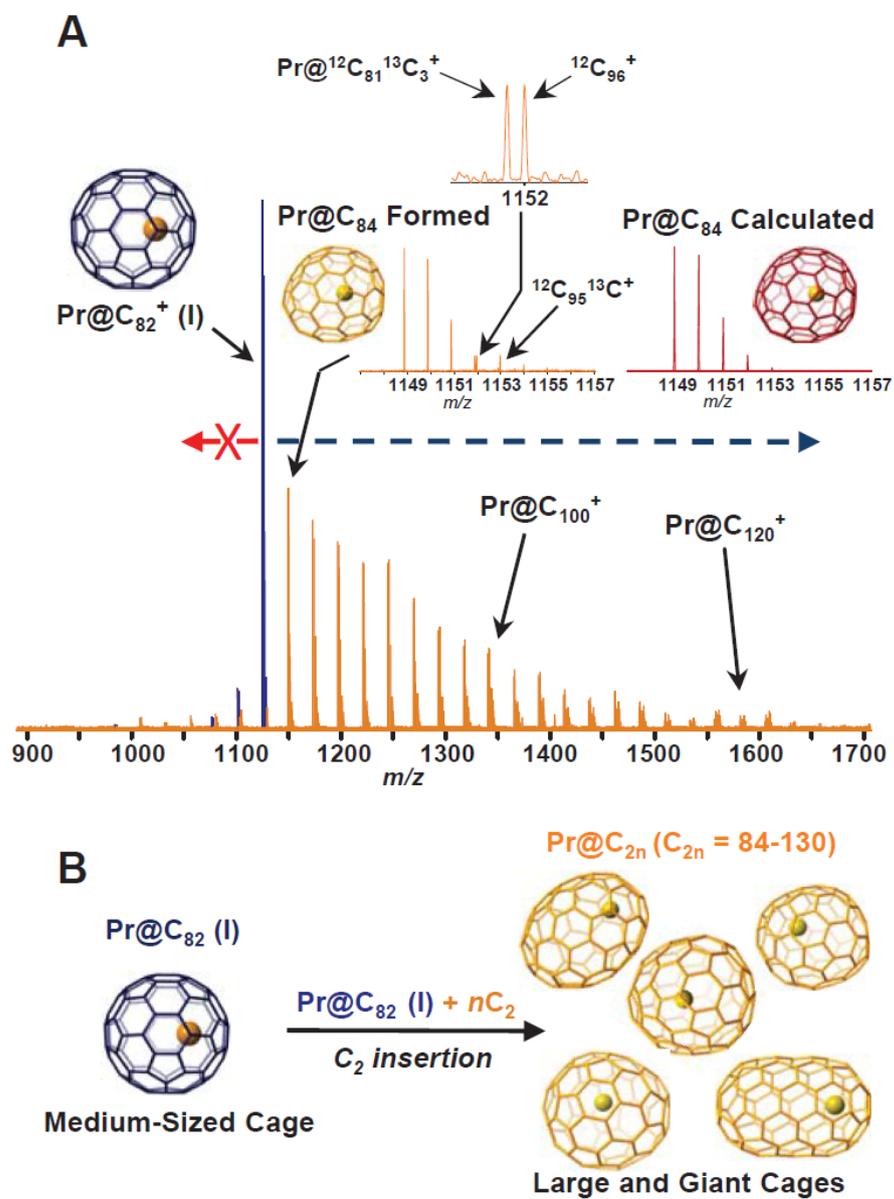


Fig.8

Figure Captions

Fig.1 Laser-vaporization supersonic cluster-beam time-of-flight mass spectrum of various lanthanum-carbon clusters. LaC_{60} is seen as an enhanced (magic number) peak [1].

Fig.2 A cross-sectional view of the third-generation DC arc discharge apparatus (the so-called Nagoya arc-discharge model) with an anaerobic collection and sampling mechanism. The produced metallofullerene-containing soot is effectively trapped by the liquid N_2 trap installed in the center of the collection chamber. Typical arc discharge conditions: 40–100 Torr He flow, 300–500 A, and 25–30 V.

Fig.3 The first X-ray diffraction evidence on encapsulation of a metal atom inside fullerene C_{82} . The MEM electron density distribution of Y@C_{82} for the (001) section. The density maximum corresponds to Y atom [3].

Fig.4 Schematic molecular structure of the $(\text{Sc}_2\text{C}_2@\text{C}_{84})$ carbide metallofullerene based on the synchrotron X-ray powder diffraction and ^{13}C NMR measurements [10].

Fig.5 Schematic dynamic structure of $\text{C}_2@\text{Sc}_2\text{C}_{84}$ as compared with the static structure $\text{Sc}_2\text{C}_2@\text{C}_{84}$ in Figure 4. The two spheres represent the Sc ions on the $\text{C}_2(z)$ symmetry axis; the y axis lies in plane of the sheet. The central part of the figure represents a superposition of carbon states as evaluated from DFTB MD calculations at 300 K [14].

Fig.6 (a) X-ray structure of the non-IPR $\text{Sc}_2@\text{C}_{66}$ fullerene, showing a top view along the C_2 axis and a side view. The equi-contour ($1.4 \text{ e}\text{\AA}^{-3}$) surface of the final MEM electron density is shown; the Sc_2 dimer is in red and the two pairs of fused pentagons are evident. (b) Schematic representation of $\text{Sc}_2@\text{C}_{66}$ [19].

Fig.7 Direct evidence of the bottom-up growth of endohedral metallofullerenes. (a) Larger $\text{La}_2@\text{C}_{2n}$ endohedral fullerenes are formed after exposure of $\text{La}_2@\text{C}_{80}$ to carbon vapour by laser ablation (50 mJ cm^{-2}) of a $\text{La}_2@\text{C}_{80}$ -coated graphite rod; (b) Laser irradiation (50 mJ cm^{-2}) of $\text{La}_2@\text{C}_{80}$ without exposure to carbon vapour. An encapsulated La atom can be ejected to form La@C_{80} and C_2 loss-fragment ions. When exposed to carbon vapour, this small amount of La@C_{80} formed will grow by the CNG mechanism (rather than fragment) to produce the very weak La@C_{80+2n} signals in a [25].

Fig.8 Bottom-up growth of large mono-metallofullerenes from $\text{Pr@C}_{2v}\text{-C}_{82}$. (a) FT-ICR mass spectrum of cluster cations after reaction of Pr@C_{82} with carbon vapor evaporated from graphite in a low-pressure He atmosphere; (b) C_2 incorporation reaction scheme with possible structures of the larger EMFs. The starting material is shown in blue, whereas bottom-up formation products are shown in orange [25].