

Endometallofullerenes in the Gas Phase: Progress and Prospect

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Abstract: This review describes the progress of the gas-phase study of endometallofullerenes (EMFs) by mass spectrometry and theoretical calculation over the past 15 years. The attention herein focuses on the gas-phase syntheses, reactions, and generation mechanisms of some novel EMF ions, along with their structures and properties. The highlighted new species include EMFs with small-size carbon cages of C_{2n} ($n < 60$), multiple metal atoms ($M_x@C_{2n}$, $x \geq 3$), late transition metals, and encaged ionic bonds. Furthermore, the gas-phase experimental and calculational supports for top-down or bottom-up models are summarized and discussed. These gas-phase results not only provide experimental evidence for the existence of related novel EMF species and possible synthesis methods for them, but they also provide new insights about chemical bonds in restricted space. In addition, the opportunities and further development directions faced by gas-phase EMF study are anticipated.

Keywords: endometallofullerenes; gas phase; electronic properties; mass spectrometry



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1. Introduction

Interestingly, the history of endometallofullerenes (EMFs) is almost as long as that of fullerene [1,2]. Just one week after the wonderful experiment on the magic cluster ion of C_{60}^+ , ions of LaC_{2n}^+ ($2n = 46-70$) were observed in the laser ablation mass spectrum of the La-loaded graphite by Smalley and his co-workers. The endohedral structure proposal was further supported by the “shrink wrapping” experiment and reaction test with oxygen or ammonia gas [3,4]. About six years later, which is one year after the success of the synthesize of solid C_{60} [5], solid EMFs of $La@C_{82}$ and $La_2@C_{80}$ were also synthesized by the laser ablation method and the Krätschmer–Huffman method [4,6]. The number of known EMFs has been rapidly and constantly growing in the past twenty years, which is mainly attributed to the improvement of synthesis, separation, and analysis methods [7–10]. Carbon cages are now able to encapsulate metal atoms in different forms, such as metallic nitrides, oxides, sulfides, and carbides. Because the cage can serve as an ideal nanoscale container for research on exceptional structures and unique clusters or chemical bonds, EMFs have great potential for showcasing new physical and chemical properties, as well as molecular devices [11–14].

However, due to the great success and rapid development of solid-state synthesis technology for EMFs, there was a time when interest in gas-phase EMF studies decreased. Notably, progress in new materials such as graphene and mass spectrometry technology bring new opportunities for gas-phase research on EMFs [15]. It can be seen that in the past 15 years, gas-phase EMF study has mainly focused on two aspects. The first one is the discovery of novel EMFs, which are difficult to prepare using existing methods and are often considered very difficult or impossible to generate, such as EMFs with small cages, with multiple metal atoms, and with transition metals or ionic bonds. This type of research can inform researchers about the stability of these novel EMFs and provide methodological recommendations for their synthesis. The second one is the generation mechanism of EMFs, which helps us to understand the generation process of EMF in principle and provides

guidance for new methods aimed at EMF synthesis. Both aspects will be summarized and discussed in this review. In summary, we focus on the discovery of new endohedral species in gas-phase experiments, which is typically related to the method of laser ablation mass spectrometry. The structures and properties of important species, mostly based on theoretical calculations, are also included. The mechanisms of generation of these novel EMFs are summarized and discussed in the last section, and an outlook on the prospects of gas-phase EMF studies is presented, too.

2. Experimental Method

From both historical and practical perspectives, gas-phase EMF study is mainly performed with mass spectrometry technology, combined with different cluster ion sources. Considering the diversity of ion species generated and the isotopic distribution of ions, high-resolution mass spectrometry is necessary in these experiments. Although high-resolution time-of-flight mass spectrometers are also applied, more experiments are conducted on Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometers, which have higher resolution and stronger capabilities for ion trapping and manipulation [16]. For the generation of the EMF ions to be studied, the Smalley-type laser-vaporization supersonic expansion cluster beam source is widely used, and there are also many kinds of variations of this type of source [1,2,17]. Generally, a rotatable solid target disk is vaporized by a focused beam from a YAG laser at 532 nm. In the source, pulsed helium gas should be adjusted in timing and pressure to coincide with the laser shot. However, there are also other cluster sources based on laser ablation in vacuum without using the accompanying pulsed helium gas. Two typical experimental setups applied by Dunk et al. in Florida State University [18–20] and Kong et al. in Nankai University [21–23] are shown in Figure 1a,b, respectively. In Dunk et al.'s setup, the cluster source block (shown in the upper corner of Figure 1a) includes vertical channels for helium gas and the laser beam. The other channel, located downstream from the target, is aligned with the gas channel to fulfill the free jet expansion and introduction of clusters into octopoles after the skimmer [18]. Dissimilarly, Kong et al. directly applied a commercial-matrix-assisted laser desorption/ionization (MALDI) [24] source for the laser ablation experiments without modifying any hardware [23]. In their experiments, the precursor was deposited on a metal plate (the MALDI plate) in turn. A focused 355 nm YAG laser beam was applied. Although a pulsed valve is also used in the source chamber (Figure 1b), its function is mainly to help in the accumulation of the generated ions in the hexapole. It is worth noting that although both experimental devices were implemented on FT-ICR mass spectrometers, the EMF species produced and the dependence of their yields on experimental conditions vary in the two setups due to their different cluster source designs and precursor materials used. This will be reflected in the examples mentioned in the following sections. For the generated EMF ions, they can be mass selected in the cell with the method of stored waveform inverse Fourier transform (SWIFT) [25] and can be further studied by other tandem mass spectrometric methods, including collision-induced dissociation (CID), ultraviolet photodissociation (UVPD), or reaction tests with reactive gas molecules (for example, O₂) [3,4,26].

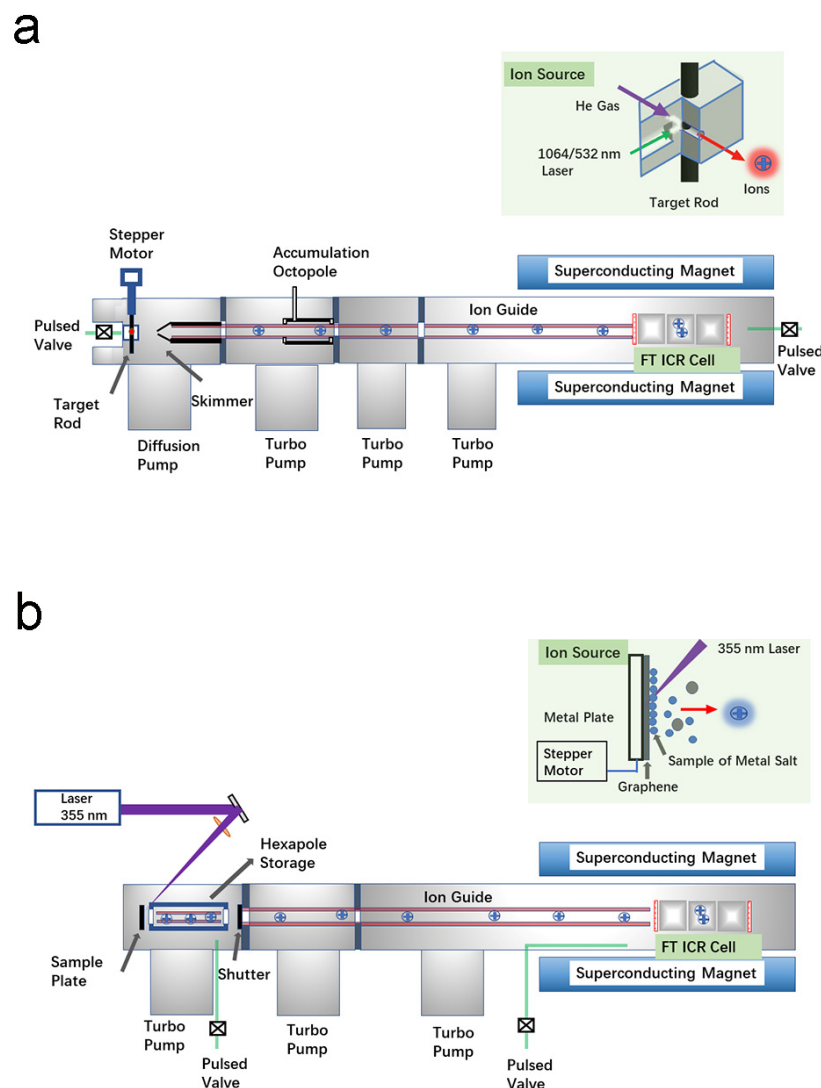


Figure 1. (a) Experimental setup for gas-phase EMF studies applied at Florida State University [18–20]. A 9.4 T FT-ICR mass spectrometer combined with a self-designed cluster source was applied. The cut-away view of the source block is shown in the upper right of the graph. The vaporization of target rods is achieved by laser shots at 532 nm, in conjunction with the opening of the pulsed valve. (b) Experimental setup for gas-phase EMF study applied in Nankai University [21–23]. A 7.0 T FT-ICR mass spectrometer with a commercial ion source (Varian IonSpec ProMALDI) was applied in these experiments without any modification. The precursor is deposited on the metal plate and irradiated by the 355 nm laser. The metal plate is controlled by a stepper motor and moves in the x–y plane during experiments.

3. Novel EMFs in the Gas Phase

3.1. EMFs with Small-Size Carbon Cages of C_{2n} ($n < 60$)

As closed-cage carbon molecules, the theoretically predicted smallest fullerene is C_{20} . However, for a very long time, questions regarding the existence of this structure have been raised due to its high curvature and reactivity. Prinzbach et al. reported the short-lived species $C_{20}Br_{20}$ in 1993 [27] and showed in 2000 that the fullerene C_{20} with a cage structure can be produced from $C_{20}HBr_{13}$ by gas-phase debromination [28]. Calculation examples show that doping the metal atoms in C_{20} can change its electronic structure [29–35]. On the other hand, Tomanek and Schluter predicted that closed carbon cages show a larger stability than other structures for clusters with sizes larger than 20, based on their theoretical calculations [36], and later Kent et al. predicted that the smallest

stable fullerenes should be the C_{26} and C_{28} clusters [37]. Thus, the possible stabilization of C_{28} by an endohedral species has been a very intriguing topic and has attracted the interest of many researchers [33,38–43]. The first experimental evidence in support of the idea was reported by Smalley et al. in 1992, in which they investigated the mass spectra of soot prepared by laser furnace and arc discharge methods [43]. Shrink-wrapping experiments indicated their endohedral structures, in which the fragmentation of larger endohedral uranofullerenes appeared to dissociate by only C_2 loss. The authors claimed that a tetravalent internal metal atom could donate four electrons to the fullerene to afford a closed-shell $M^{4+}@C_{28}^{4-}$ species with a large HOMO–LUMO gap and permit sufficient stabilization for such species [43].

By using a pulsed laser vaporization cluster source, Kroto and Marshal et al. have also reported that C_{28} fullerene could be stabilized by encapsulation with appropriate metal forms [44]. Impressively, for the first time, they reported the high-resolution mass spectrum of $Ti@C_{28}$ (Figure 2). For a long time, titanium has been one of the most attractive tetravalent candidates for C_{28} stabilization by encapsulation. However, its major isotope, ^{48}Ti , which is just 52 mDa different in mass from C_{44} , makes the ion of $Ti@C_{28}$ hard to resolve from the signal of empty-cage C_{32} with conventional mass spectrometers. Using a 9.0-T Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR) mass spectrometer, Kroto and Marshal et al. clearly identified the species, along with ions of $Ti@C_{2n}$ ($n = 19–23$), in the mass spectrum [44]. Collision-induced dissociation (CID) experiments on $Ti@C_{28}$ show that the ion can remain completely intact with neither the loss of Ti nor the loss of C_3 or C after many collisions, indicating the fact that the metal is not directly attached to the skeleton, which is neither linear nor cyclic. Further CID experiments on $Ti@C_{30}$ show that $Ti@C_{30}$ can fragment to $Ti@C_{28}$ by C_2 loss, demonstrating that both species are endohedral. They also investigated other metal elements in the periodic table and found that both $Zr@C_{28}$ and $U@C_{28}$ formed in abundance, but $Hf@C_{28}$ was much weaker.

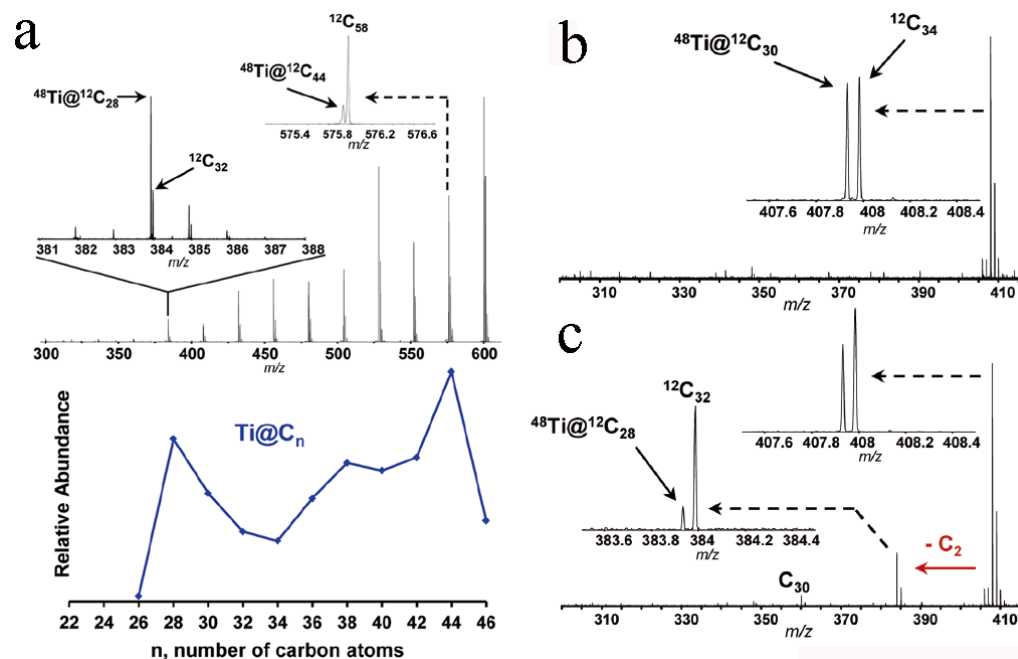


Figure 2. (a) Laser vaporization mass spectrum of a Ti-doped graphite target. Among the observed cations in the $Ti@C_{2n}$ family, $Ti@C_{28}$ is observed in great abundance without the accompany of the empty-cage C_{28} . (b) Isolated ions of $Ti@C_{30}$ and C_{34} , and (c) fragmentation pathway of $Ti@C_{30}$. Taken with permission from [44].

Dunk et al. have synthesized a series of uranium-endohedral fullerenes using the method of Krätschmer–Huffman arc discharge [45]. Several uranofullerenes were able

to be observed in experiments utilizing solvents with different polarities. Via extractions using pyridine and 1,2-Dichlorobenzene (o-DCB), species of $U@C_{2n}$ ($2n = 28, 60, 66, 68$, and 70) were observed in the FT-ICR mass spectra. The distribution of the series of uranium-endohedral fullerenes was found to be different from that obtained in the early experiment reported by Smalley and his colleagues [43]. Some missing species of uranium-endohedral fullerenes have been observed for the first time in Dunk et al.'s experiment [45].

Due to its primary oxidation state at +4, it was predicted that thorium could form $Th@C_{28}$ via the method described above. However, Dunk et al. found that the species $Th@C_{28}$ was absent and replaced by the species $Th@C_{36}$ in the resulting mass spectrum, which could be attributed to the larger ionic radius of Th^{4+} relative to U^{4+} [20]. For the purpose of creating mono-metallofullerene from metal-incorporated graphite, more than 80 components were examined separately in their experiment. The detectable species with the smallest carbon cages are $M@C_{50}$ for Group 1 elements (K, Rb, Cs), $M@C_{42}$ or $M@C_{44}$ for Group 2 elements (Ca, Sr, Ba), $M@C_{36}$ for trivalent rare earth metals (Sc, Y, La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, Lu), $M@C_{44}$ for divalent lanthanides (Sm, Eu, Yb), and $M@C_{50}$ for Ga and In. The results indicate that the oxidation states of the encapsulated metals (corresponding to the charge transfer to the carbon cage outside) and the ionic radius are determining factors that govern the size limits of the observed EMFs and the corresponding EMF formation.

Alternatively, Rodríguez-Forte et al. recently reported the cation species of $U@C_{2n-1}B$ ($2n - 1 = 27-59$) using their laser vaporization source [46]. As shown in Figure 3, mass spectrometric results identified the boron-doped $U@C_{27}B$ as the most prevalent borafullerene within the $U@C_{2n-1}B$ family. According to density functional theory (DFT) calculations, the U atom is positioned in the middle of the cage and interacts with every other atom there as though it were a 28-hapto ligand. This exotic radical shows us an intriguing example of unique host–guest chemistry in metallofullerenes.

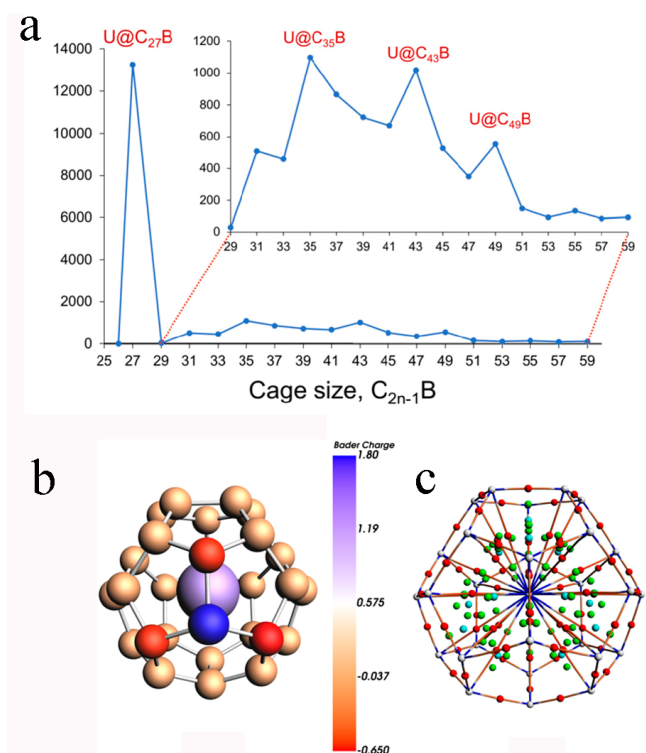


Figure 3. (a) Distribution of cations of $U@C_{2n-1}B^+$ formed by laser vaporization of U-containing graphite. The region $2n - 1 = 29$ to 59 is expanded in the inset for clarity. (b) Bader charges and (c) AIM critical points (CPs) and bond paths for $U@C_{27}B$. Atom CP in white, bond CP in red, ring CP in green, and cage CP in light blue. Taken with permission from [46].

The observed new EMF species in small carbon cages in the gas phase were also simulated using theoretical methods on their structure and properties [31–35,47–49]. For example, Rodríguez-Forte, Kroto, and Poblet and have reported their theoretically calculated results of the Ti@C_{2n} ($2n = 26–50$) family [47]. The stability and unique electronic characteristics of the two main species, Ti@C_{28} and Ti@C_{44} , account for their abundance. It is demonstrated that all of the optimum isomers in the family are connected by a straightforward C_2 insertion, with the exception of a few cages that need an extra C_2 rearrangement. Da et al. studied the ground-state electronic structures of U@C_{28} in its neutral, monovalent, and bivalent cationic forms [41]. The findings indicate that, rather than the $(5f)^1(\text{cage})^1$ ground state with a D_2 symmetry, the neutral U@C_{28} is characterized by a $(\text{cage})^2$ ground state with a T_d symmetry [41]. Meng et al. studied the geometric and bonding properties of EMFs, including an f-block metal atom or ion enclosed in a C_{20} cage [48]. Muñoz-Castro investigated the availability of $\text{U}_2\text{@C}_{36}$ as an example for the small endohedral dimetallofullerene. The result indicates its neutral and dicationic forms can behave as plausible candidates with a U-U distance of 2.27 Å [49]. Zhou et al. reported the structures and properties of TM@C_n ($n = 20, 24, 28$) based on their DFT calculations, showing that after the embedding of TM atoms, the stability of TM@C_{20} is greatly enhanced [33]. Their recent results show that the general species of $\text{Mg}^{2+}\text{@[C}_{20}]^{n-2}$ can be classified as superatoms [35].

3.2. EMFs including Multiple Metal Atoms ($\text{M}_x\text{@C}_{2n}$, $x \geq 3$)

The Coulomb repulsion among the metal ions in EMFs with multiple metal atoms creates a barrier to their stabilities. As the number and size of metal atoms increase, this situation becomes more serious. There are two ways to solve the problem [50]. One is to introduce electronegative elements (such as N, S, and O) to compensate for the Coulomb repulsion; the other is to adopt fullerene cages with large sizes. For the generation and structure study of EMFs that include multiple metal atoms, gas-phase experiments provide a convenient and effective method, especially when combined with DFT calculations. Graphene has been found to be a powerful precursor for the generation of EMF ions that encage multiple metal atoms in the gas phase [23,51–58]. For example, the laser ablation of LaCl_3 /graphene can generate EMF ions of $\text{La}_n\text{@C}_{2m}^+$ with a long accumulation time in the cell of the FT-ICR mass spectrometer [53]. As shown in Figure 4a, compared to the wide distributions of $\text{La@C}_{58–194}^+$ and $\text{La}_2\text{@C}_{74–168}^+$, the distribution of trimetallofullerene ions is narrower ($2n = 96–160$), with a center located at $\text{La}_3\text{C}_{110}$. The primary products are the monometallofullerene ions; nonetheless, the species ranked second in abundance is La_3C_{2m} , instead of La_2C_{2m} . Other EMF ions of $\text{La}_4\text{C}_{112–160}$, La_5C_{2m} ($132 \leq 2m \leq 170$), and La_6C_{2m} ($152 \leq 2m \leq 180$) ions were also identified.

Although the diverse species generated in these experiments make the clear isolation of a special EMF ion difficult, the CID experiments have also been applied to some EMF ions, such as CaC_{60}^+ , SrC_{60}^+ , BaC_{60}^+ , BaC_{92}^+ , and BaC_{130}^+ [23]. For other EMF ions with more metal atoms or larger carbon cages, the gas-phase oxygen reaction test was applied to verify their endohedral structures. Nevertheless, since endohedral carbide cluster fullerene structures cannot be ruled out, it is not possible to properly identify their structures based solely on these mass spectrometric experiments.

The laser ablation of the mixture of graphene and LuCl_3 generated EMF ions with more metal atoms encaged (Figures 4b and 5) [54]. As shown in Figure 5, EMF ions of $\text{Lu}_n\text{C}_{2m}^+$ ($n = 1–9$, $50 \leq 2m \leq 198$) were observed in the mass spectrum. The gas-phase reaction test experiments confirmed their endohedral architectures. A few mono-EMF ions, such as LuC_{50}^+ and LuC_{66}^+ , exhibit appreciable relative intensities, suggesting that the encaged metal atom significantly stabilizes relative IPR-violating cages. Similar to the cases of La and Y, the yield of trimetallofullerene ions, $\text{Lu}_3\text{C}_{2m}^+$, is the highest among all of the multimetallic metallofullerene ions. The intensities of $\text{Lu}_4\text{C}_{2m}^+$ and $\text{Lu}_5\text{C}_{2m}^+$ are still strong, suggesting the potential of their practical synthesis. The more Lu atoms contained in the EMFs, the larger the required carbon cage size. It has been found that the cage's average size rises by 12 carbon atoms for every additional Lu atom within the fullerene.

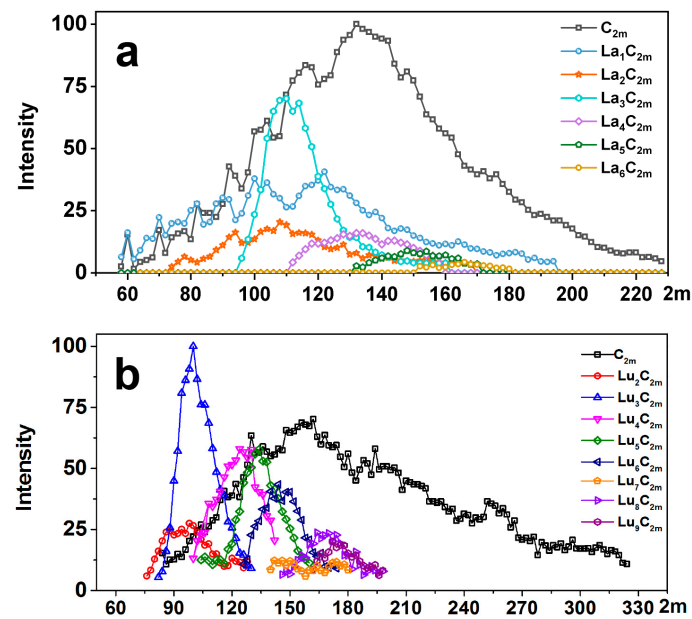


Figure 4. Intensity distributions of (a) $\text{La}_{1-6}\text{C}_{2m}^+$ and (b) $\text{Lu}_{2-9}\text{C}_{2m}^+$. (Figure 4b is taken with permission from [54]).

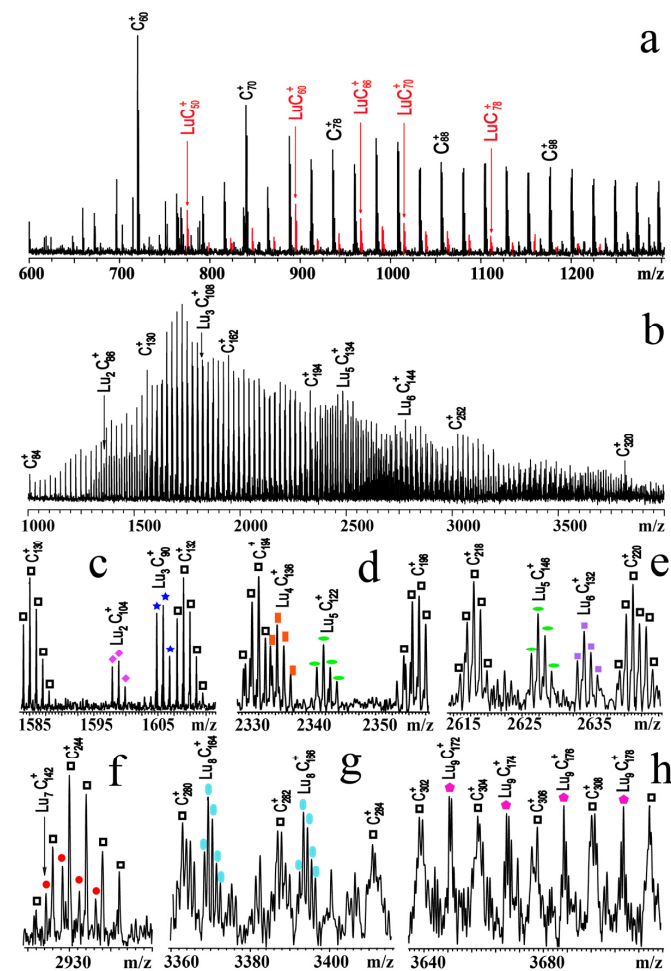


Figure 5. Laser ablation mass spectra of $\text{LuCl}_3/\text{graphene}$ (a) obtained in the m/z region of 600–1300, and (b) obtained in the m/z region of 1000–4000. Some metallofullerene ions of $\text{Lu}_{2-9}\text{C}_{2n}^+$ are further shown in (c–h) in detail. Taken with permission from [54].

Other rare earth metals were also considered in order to obtain a general understanding of the multi-metallofullerene ions generated by laser ablation. Together with the previous data for alkali metal and alkali earth metal species, Table 1 summarizes all the multi-metallofullerene species created under identical experimental conditions in such studies [23,52–55]. As shown here, EMF ions with numerous metal atoms ($n > 4$) are only available in the cases of Y, La, Tb, Ho, and Lu. The increased number of encaged metal atoms also creates requirements for the size of carbon cages, but these requirements vary for different metals. For instance, the distribution of $\text{La}_5\text{C}_{2m}^+$ falls between 132 and 170 in terms of $2m$, whereas the ranges for Tb, Ho, and Lu are 124 and 150, 114 and 160, and 104 and 160, respectively. The outcomes show the impacts of the metals' ionic radii in addition to the interaction of metal clusters with carbon cages. For the majority of these rare earth metals, it is possible to generate distinct multi-EMF ions ($n \geq 2$); however, Sm and Eu exhibit divergent outcomes, with no metallofullerene ions reported in the studies. For alkali metals and alkaline earth metals, only dimetallofullerene ions were observed in the examples of calcium and barium.

Table 1. Observed multi-metallofullerene ions of different metals in gas-phase laser ablation experiments.

M	Oxide States	Observed Multi-Metallofullerene Ions	Ref.
La	+3	$\text{La}_2\text{C}_{74-168}^+$, $\text{La}_3\text{C}_{96-160}^+$, $\text{La}_4\text{C}_{112-160}^+$, $\text{La}_5\text{C}_{132-170}^+$, $\text{La}_6\text{C}_{152-180}^+$	[53]
Ce	+3 +4	$\text{Ce}_2\text{C}_{88-106}^+$, $\text{Ce}_3\text{C}_{94-136}^+$, $\text{Ce}_4\text{C}_{100-150}^+$	[55]
Pr	+3 +4	$\text{Pr}_2\text{C}_{88-102}^+$, $\text{Pr}_3\text{C}_{94-134}^+$, $\text{Pr}_4\text{C}_{108-138}^+$	[55]
Nd	+3	$\text{Nd}_3\text{C}_{96-130}^+$	[55]
Sm	+2 +3	None	[55]
Eu	+2 +3	None	[55]
Gd	+3	$\text{Gd}_2\text{C}_{86-108}^+$, $\text{Gd}_3\text{C}_{90-128}^+$, $\text{Gd}_4\text{C}_{106-134}^+$	[55]
Tb	+3 +4	$\text{Tb}_2\text{C}_{80-112}^+$, $\text{Tb}_3\text{C}_{86-130}^+$, $\text{Tb}_4\text{C}_{100-144}^+$, $\text{Tb}_5\text{C}_{124-150}^+$, $\text{Tb}_6\text{C}_{134-164}^+$, $\text{Tb}_7\text{C}_{148-176}^+$	[55]
Dy	+3	$\text{Dy}_2\text{C}_{82-108}^+$, $\text{Dy}_3\text{C}_{90-128}^+$	[55]
Ho	+3	$\text{Ho}_2\text{C}_{74-104}^+$, $\text{Ho}_3\text{C}_{86-124}^+$, $\text{Ho}_4\text{C}_{98-112}^+$, $\text{Ho}_5\text{C}_{114-154}^+$, $\text{Ho}_6\text{C}_{132-162}^+$	[55]
Er	+3	$\text{Er}_2\text{C}_{82-96}^+$, $\text{Er}_3\text{C}_{90-114}^+$	[54]
Tm	+2 +3	$\text{Tm}_2\text{C}_{80-100}^+$, $\text{Tm}_3\text{C}_{88-122}^+$, $\text{Tm}_4\text{C}_{110-132}^+$	[54]
Yb	+2 +3	$\text{Yb}_3\text{C}_{90-110}^+$	[54]
Lu	+3	$\text{Lu}_2\text{C}_{76-128}^+$, $\text{Lu}_3\text{C}_{82-130}^+$, $\text{Lu}_4\text{C}_{100-142}^+$, $\text{Lu}_5\text{C}_{104-160}^+$, $\text{Lu}_6\text{C}_{126-174}^+$, $\text{Lu}_7\text{C}_{140-180}^+$, $\text{Lu}_8\text{C}_{146-198}^+$, $\text{Lu}_9\text{C}_{172-198}^+$	[54]
Y	+3	$\text{Y}_2\text{C}_{74-130}^+$, $\text{Y}_3\text{C}_{88-128}^+$, $\text{Y}_4\text{C}_{102-142}^+$, $\text{Y}_5\text{C}_{128-154}^+$, $\text{Y}_6\text{C}_{130-154}^+$	[53]
Li	+1	None	[52]
Na	+1	None	[52]
Rb	+1	None	[52]
Cs	+1	None	[52]
Mg	+2	None	[23]
Ca	+2	$\text{Ca}_2\text{C}_{96-160}^+$	[23]
Sr	+2	None	[23]
Ba	+2	$\text{Ba}_2\text{C}_{80-182}^+$	[23]

3.3. EMFs including Late Transition Metals

Although EMFs with rare earth metals and their adjacent elements (groups I–IV) have been investigated in the gas phase, those containing post-transition metals are very rarely experimentally studied. Entrapping these transition metals in fullerene cages is still a challenge [56]. There may be many reasons for this, but one of them is that these metal species usually exhibit high reactivity with carbon atoms during the generative process. Thus, it is suggested that the most performable way to make EMFs containing post-transition metals is to use heterometal clusters to reduce the reactivity of these metal species.

Recently, Kong's group successfully synthesized metal fullerene ions containing platinum atoms in the gas phase for the first time [56]. By laser ablation of a mixed sample of graphene/ LaCl_3 / PtCl_4 in vacuum, the EMF ions of $\text{La}_m\text{PtC}_{2n}^+$ were observed (Figure 6a) and verified with oxygen reaction tests [50,56]. An example is shown in Figure 6. Apart from the EMF ions of $\text{La}_2\text{C}_{2n}^+$ and $\text{La}_3\text{C}_{2n}^+$, $\text{La}_m\text{PtC}_{2n}^+$ ($m = 2-3$; $n = 43-65$) was also observed. The distributions of the observed EMF ions are compared and shown in Figure 6b. It can be found that EMF ions of $\text{La}_2\text{PtC}_{2n}^+$ have a distribution from $2n = 86$ to 114 centered

on the $\text{La}_2\text{PtC}_{98}^+$, and those of $\text{La}_3\text{PtC}_{2n}^+$ have a distribution from $2n = 98$ to 130 centered on the $\text{La}_3\text{PtC}_{112}^+$.

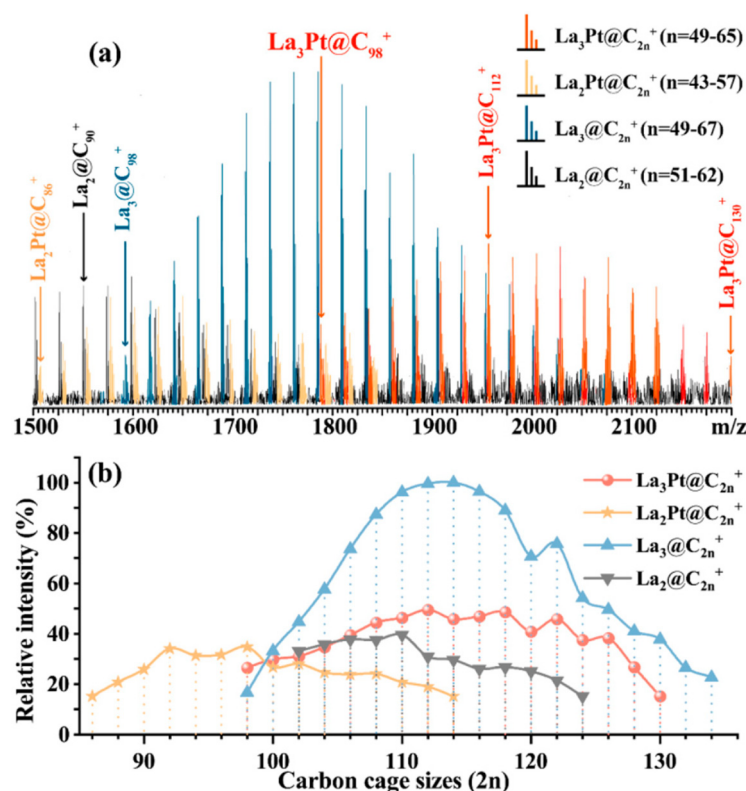


Figure 6. (a) Laser ablation MS spectrum of the mixture of graphene/ LaCl_3 / PtCl_4 in the region of 1500–2200 m/z . For convenience, the abundant fullerene ions of C_{2n}^+ ($n = 63$ –91) have been manually removed. (b) Intensity distributions of $\text{La}_m\text{Pt@C}_{2n}^+$ ($m = 2, 3$) and $\text{La}_m\text{@C}_{2n}^+$ ($m = 2, 3$) observed in the upper figure. Taken with permission from [50].

Extensive theoretical studies have been performed for the neutral forms of these two selected species, $\text{La}_2\text{PtC}_{90}^+$ and $\text{La}_3\text{PtC}_{98}^+$ [50,56]. For $\text{La}_2\text{PtC}_{90}^+$ (the neutral species of $\text{La}_2\text{PtC}_{90}^+$), the two most stable structures are $\text{La}_2\text{Pt@C}_2(99915)\text{-C}_{90}$ and $\text{La}_2\text{Pt@C}_2(99916)\text{-C}_{90}$, with the energy of the latter being 8.1 kcal/mol greater than that of the former. Moreover, large HOMO-LUMO gaps of 1.28 and 1.13 eV have been found for the two isomers. Impressively, the most stable isomer of the corresponding metal carbide EMFs, which has been identified to be $\text{La}_2\text{PtC}_2@D2(81738)\text{-C}_{88}$, has a much higher energy (>89 kcal/mol) than $\text{La}_2\text{Pt@C}_2(99915)\text{-C}_{90}$. As shown in Figure 7a,b, the internal La_2Pt clusters in both structures exhibit a “V” shape, with La coordinating with the carbon cage and Pt located at the center of the La_2Pt cluster, serving as a connecting point to stabilize the EMFs. Within the triatomic cluster, the distances between La–La and La–Pt are ~ 4.01 and 2.73 Å, respectively, indicating the existence of the La–Pt bond.

The two most stable isomers of $\text{La}_3\text{Pt@C}_{98}$ were found to be $\text{La}_3\text{Pt@C}_2(231010)\text{-C}_{98}$ and $\text{La}_3\text{Pt@C}_1(231005)\text{-C}_{98}$ [50]. Their structures are shown in Figure 7c,d. In both isomers, the La_3Pt clusters form pyramidal tetrahedrons in carbon cages. The distances between two nearby La atoms are 4.18 – 4.40 Å, a little longer than those in the top two isomers of $\text{La}_2\text{Pt@C}_{90}$. The encaged clusters of La_3Pt in both isomers have typical La–Pt bonds with a length of about 2.80 Å, and La–Pt–La bond angles of $\sim 100^\circ$, with a shape similar to the metal nitride clusters in $\text{M}_3\text{N@C}_{80}$ ($M = \text{Y, Tb, Gd}$), but different from planar triangles in the cases of $\text{M}_3\text{N@C}_{80}$ ($M = \text{Sc, Lu, Dy}$).

In order to explore the role of the encaged Pt atom, Mulliken charge distribution calculations were carried out for these structures [50,56]. Results show that the carbon cages and the endohedral La atoms are negatively and positively charged, respectively.

Very interestingly, it is noted that Pt atoms within La_2Pt or La_3Pt clusters appear to have a negative valence and may mediate the interactions between two La or among three La atoms. For $\text{La}_2\text{Pt}@C_2(99915)\text{-C}_{90}$, the charges of the two La atoms are +1.82 and +1.81, and the Pt atom is negatively charged (with a charge of -0.64). This role is similar to that of Pt in the embedded tetrametallic fullerene $\text{La}_3\text{Pt}@C_{98}$. For both $\text{La}_3\text{Pt}@C_1(231005)\text{-C}_{98}$ and $\text{La}_3\text{Pt}@C_2(231010)\text{-C}_{98}$, the La atoms present positive states (from 0.49 to 0.52), while the Pt atoms are negatively charged (around -0.24). In the case of $\text{La}_3\text{Pt}@C_{98}$, all three of the La atoms create 2c–2e bonds with the negatively charged Pt atom, which serves as a mediator. Interestingly, the entire molecule is stabilized by the 4c–2e tetrametallic bond, with the highest occupancy number in the unit of La_3Pt . It is noteworthy that seven electrons have transferred from the inner metal cluster to the outside fullerene cage in this instance, which is quite rare and has not been documented before. This is further evidenced by the adaptive natural density partitioning (adNDP) analysis, where Pt takes two electrons to fill its 5d-shell from La atoms and shares its $6s^2$ pair as a back-donation with La atoms, resulting in its unique electron distribution in a form of $[(\text{La}^{3+})_3\text{Pt}^{2-}]^{7+}@C_{98}^{7-}$.

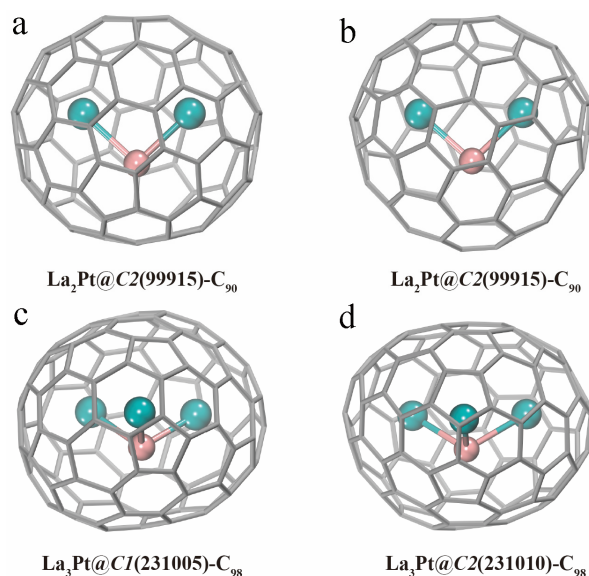


Figure 7. The calculated structures of two most stable isomers of $\text{La}_2\text{Pt}@C_{90}$: (a) $\text{La}_2\text{Pt}@C_2(99915)\text{-C}_{90}$, (b) $\text{La}_2\text{Pt}@C_2(99916)\text{-C}_{90}$. The calculated structures of the two most stable isomers of $\text{La}_3\text{Pt}@C_{98}$: (c) $\text{La}_3\text{Pt}@C_1(231005)\text{-C}_{98}$ and (d) $\text{La}_3\text{Pt}@C_2(231010)\text{-C}_{98}$.

3.4. EMFs including Ionic Bonds

There are still big challenges to encapsulating various ionic bonds in fullerenes (except for metal oxides) [57–61]. The confinement of an individual ionic bond is very difficult, since it has neither sharing electrons nor a fixed pairing relationship between the two ions. Due to the difficulty in generation, they have only very rarely been the subject of experimental research. Using a Smalley-type ion source, Martin et al. observed such fullerene ions in the gas phase in their pioneering works. They identified ions of $\text{CaCl}@C_{66}^+$ and $\text{HoCl}@C_{60}^+$ in the gas phase and gave a justification for the species' threshold sizes using the spherical approximation [61].

Recently, Kong's group reported the identification of endohedral ions of LuClC_{2n}^+ ($2n = 90\text{--}190$) with high-resolution laser ablation mass spectrometry [57]. In the experiments, a mixture of graphene/ LuCl_3 / LiCl was applied as the precursor, and oxygen gas was used as the reaction gas to verify their endohedral structures. Similarly, mixtures of graphene and sodium halides (NaX) ($X = \text{Cl}, \text{Br}, \text{I}$), EMF ions of $\text{NaCl}@C_{2n}^+$ ($2n = 120\text{--}244$), $\text{NaBr}@C_{2n}^+$ ($2n = 110\text{--}240$), and $\text{NaI}@C_{2n}^+$ ($2n = 116\text{--}198$) were also observed by the same group [58]. Interestingly, Li or K could not substitute for the encapsulated metal ion in

these studies, indicating that the metal cation's effects on the EMFs outweigh those of halide anions.

To figure out the structures and properties of the endohedral ionic bond fullerenes, the species of LuCl@C_{90} was selected and studied systematically using DFT methods [57]. $\text{LuCl@C}_2(99917)\text{-C}_{90}$ and $\text{LuCl@C}_2(99914)\text{-C}_{90}$ were found to be the top two isomers (Figure 8), which have significant HOMO–LUMO gaps of 1.61 and 1.82 eV, respectively. Statistical thermodynamic analysis shows that the former prevails inside a small temperature range of 0 to 500 K. With the temperature increasing, it is exceeded by $\text{LuCl@C}_2(99914)\text{-C}_{90}$ at 650 K and by $\text{LuCl@C}_2(99913)\text{-C}_{90}$ at 3000 K. For all optimized isomers, it was found that the Lu atoms are situated between the Cl atoms and the cages, and the Cl atoms are found in the hubs of the cages. The potential curve of an encaged ionic bond is distinct from that of isolated ionic bonds, which are identified by their usual Morse or Morse long-range potentials. As shown in Figure 7, infinite potential wells exist due to the restriction of the carbon cages, and the wells are deeper than those of unprotected ionic species, clearly showing that they have different characteristics. In addition, the calculation shows that the equilibrium distances of the Lu–Cl bonds in both isomers is 2.49 Å, which is larger than that of LuCl_2^+ (2.30 Å) and a little smaller than that of LuCl (2.55 Å).

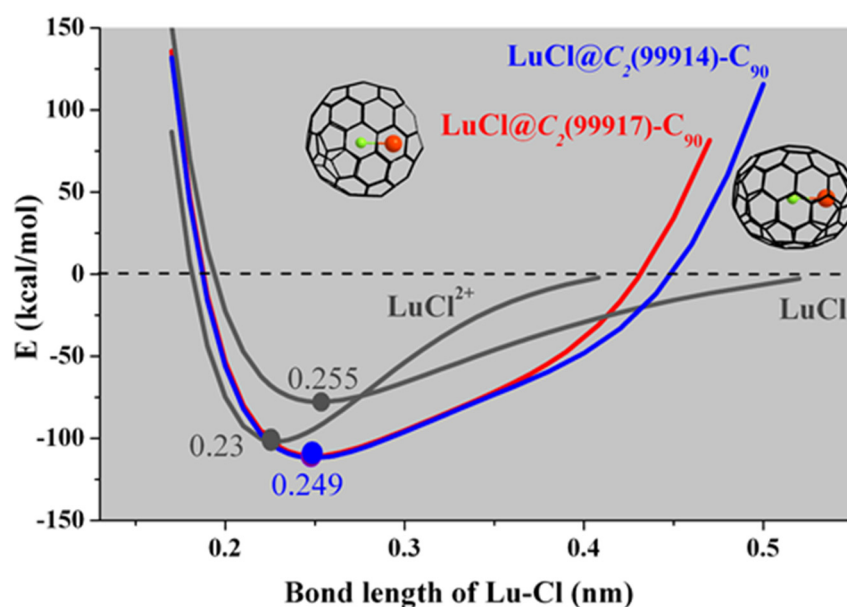


Figure 8. Potential curves of LuCl_2^{2+} , LuCl , $\text{LuCl@C}_2(99917)\text{-C}_{90}$, and $\text{LuCl@C}_2(99914)\text{-C}_{90}$. Taken with permission from Ref. [57].

An interesting effect of endohedral ionic bond fullerenes is that it is possible to rotate the bond inside the carbon cages. The energy barrier mainly depends on the interaction between the metal ion and the cage [57]. For instance, seven energy minima were discovered during the rotation of the Cl–Lu bond in the lowest energy isomer of $\text{LuCl@C}_2(99917)\text{-C}_{90}$, and the energy barriers were found in the range of 20–220 kcal/mol. However, the results depend very much on the selected plane for rotation. If the perpendicular rotation plane is selected, there are only four energy minima and the rotation energy barrier is considerably larger, reaching up to 600 kcal/mol.

In fact, the properties of encaged ionic bonds have previously been noticed by theoretical chemists and have always been a focus of their attention [62–65]. Foroutan-Nejad et al. proposed a single-molecule switch based on the neutral dipolar molecule that uses alkali metal halides contained in a C_{70} cage for data storage [65]. The encaged ionic bonds have two local energy minima separated by an energy barrier relative to the fullerene. Attractively, an external electric field can be used to manipulate the dipolar system inside the fullerene. This is possible with contemporary instruments like scanning tunneling

microscopes. The ionic bond aligns along the main axis of C_{70} to minimize the steric clash. The conformations with the dipole moment along the electric field are more stable than the others when the electric field is on. With an increasing electric field, the stabilization should lead to the reorientation of the encaged ionic bond. The same group has also proposed using a two- or four-electrode system to speed up the switching procedure, showing their potential in the application of random-access memories and memristors [64]. As illustrated in Figure 9, the dipolar MX causes the system to operate like a diode by polarizing the fullerene shell electrons. A series of species of $MX@C_{70}$ (M = a metal or hydrogen, X = a halogen or a chalcogen) have been studied to be identified as possible molecular memristors by the same research group.

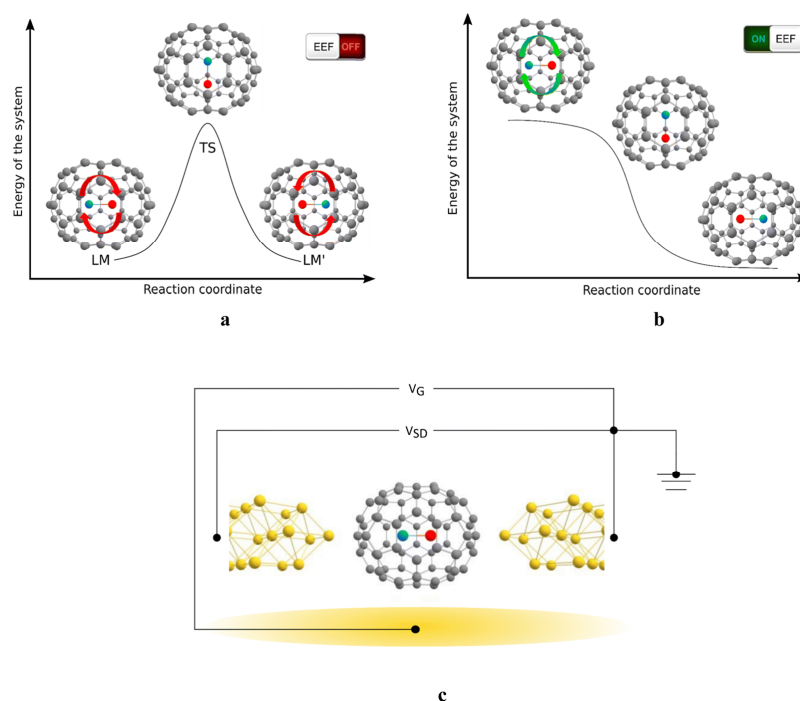


Figure 9. The principle of an $MX@C_{70}$ molecular memristor (EEF stands for the external electric field). (a) $MX@C_{70}$ with two local minima (LM and LM') separated by a transition state (TS) with an energy barrier. (b) Upon application of external voltage, one of the local minima becomes unstable. This leads to the rotation of MX between LM and LM' (or LM' and LM), and thus to the switching of the system's polarity and conductivity. (c) The four-electrode setup in which the source–drain voltage (VSD) is applied horizontally and the gate voltage (VG) is perpendicular to the VSD. Taken with permission from Ref. [64].

Impressively, Gan et al. recently reported the preparation of an open-cage fullerene as a selective molecular trap for ionic bonds of $LiF/[BeF]^+$ [60]. They made use of a hydroxy group-containing open-cage C_{60} derivative. LiF and $[BeF]^+$ were encapsulated as a result of the hydroxy group's ability to coordinate lithium or beryllium cations, functioning as a bait or hook. The whole structures were clearly identified by single-crystal X-ray diffraction. A bright future lies ahead for the development of more cage-opening reactions for the prospective uses of fullerene-based molecular containers, especially in light of the recent advancements in the logic-in-memory operations of a two-terminal single-metallofullerene device at room temperature [62].

4. Mechanism Study

Similar to those of fullerenes, the suggested mechanisms for the formation of EMFs can be generally classified into two types: bottom-up or top-down [20,44,47,66–82]. For example, Dunk et al. demonstrated that $U@C_{28}$ acts as a precursor for larger uranofullerenes

while itself being formed through a bottom-up process [44]. They have identified the structures of Ti@C_{2n} ($2n = 26\text{--}50$) and uncovered essential features in their growth processes by DFT calculations and molecular dynamics (MD) simulations [47]. Further studies by the same group show more proofs of the suggested bottom-up formation process of giant mono-EMFs from $\text{Pr@C}_{2v}\text{--C}_{82}$ [20]. They proposed that, under EMF synthesis circumstances, mono-metallofullerenes with small to giant sizes might form in the gas phase via a bottom-up mechanism. The extent of charge transferred to carbon cages appears to be determined by the elements' ionization energies during graphite/metal evaporation. It has been suggested that the unconventional small-sized EMFs could stabilize by charge transfer, although the existing strain energy resulted in the impeding of C_2 insertion and the inhibition of overall bottom-up formation of large-sized metallofullerenes. MD simulation also plays an important role in understanding the formation mechanisms of EMFs [83–87]. Using constructed multi-body potential functions, Yamaguchi et al. found that the clustering process of a system containing 500 isolated carbon atoms and five La atoms under a controlled temperature of 3000 K can result in lanthanum-containing caged clusters. For the Ni–C system, the Ni atom ultimately stayed on the face of caged structures [83]. Deng et al. investigated the effects of the inert cooling gas helium in the Sc-EMF forming process with the method of quantum chemical molecular dynamics. Their results show that Sc encapsulation involves nucleation of carbon clusters with Sc atoms at early stages, and the existence of He gas reduces the size of the self-assembled cages [84]. An extended simulation with an Fe atom shows no formation of such Fe-EMF, which is consistent with experimental results [71]. Fan et al. found that the growth patterns of Sc-EMFs resemble those of hollow cages, and the He gas could promote both the formation of carbon cages and the encapsulation of scandium atoms [86].

The bottom-up mechanism is suitable for the formation of mono-metallofullerenes from metal-incorporated graphite [20]. However, the generation of multiple metallofullerenes in some experiments, such as the examples shown in Figures 3–5, may have different mechanisms. The top-down mechanism offers another kind of possibility [71–78]. There is evidence to support the theory that giant fullerenes formed from large-size polycyclic aromatic hydrocarbons (PAHs), or graphene sheets shrunk into smaller ones, through interstellar and laboratory observations as well as theoretical calculations [71,77,78]. For example, Irle et al. use a 'shrinking hot giant fullerene' mechanism in which giant carbon cages occur first, followed by multiple C_2 losses with self-assembly to appropriate symmetric fullerene cages, such as $I_h\text{--C}_{60}$ and $D_{5h}\text{--C}_{70}$ [71]. Moreover, the transformation of graphene to a fullerene cage was demonstrated by Chuvilin et al., based on their transmission electron microscopy and theoretical studies [74].

For EMFs, the top-down mechanism is also applied in some cases [23,48–56,79–82]. Dorn et al. isolated and characterized metal carbide metallofullerenes $\text{M}_2\text{C}_2\text{@C}_1(51383)\text{--C}_{84}$ ($\text{M} = \text{Y, Gd}$) and proposed that the cage with fused pentagons is a preserved 'missing link' in the top-down mechanism [80]. The unique asymmetric structure can form many symmetric fullerenes that account for some well-known solvent-extractable metallofullerenes using limited, well-established rearrangement steps. Lu et al. presented the identified $\text{La}_2\text{C}_2\text{@C}_2(816)\text{--C}_{104}$ as an origin formation of other known ideal tubular cages by removing the pyracylene motif, providing support for the top-down formation mechanism of such fullerenes [79]. Using the method of transmission electron spectroscopy, Sinitsa et al. proposed a method for synthesis of nickel EMFs, in which the formation was initiated by electron irradiation of a metal cluster surrounded by amorphous carbon inside a carbon nanotube [87]. Their MD simulations also rationalize the experimental observations. On the other hand, Kong et al. suggested the top-down mechanism to explain the multiple EMF ions produced in the process of laser ablation of graphene flakes mixed with metal salts [23,48–56]. It is proposed that the instantaneous process of wrapping metal atoms or clusters inside curved graphene flakes produced by laser irradiation can lead to the production of EMFs with large-sized cages and multi-metal atoms. Moreover, the mechanism can be used to interpret the generation of fullerenes with encaged ionic bonds in a similar

way. It is important to notice the difference between the use of graphene and graphite as precursors in these experiments, since their differently reported mass spectra indicate their different laser ablation processes and mechanisms.

5. Prospect

The gas-phase EMF study provides valuable information in many ways. The importance of gas-phase research on EMFs in their discovery can never be overstated, and they are going to remain essential in interdisciplinary investigations of new species in this big family. In this review, we summarized the progress of gas-phase EMF studies in the past 15 years, focusing on novel EMF species identified in the gas phase and the relative mechanism study, which provided valuable information for the structural research, synthesis, and design of such new molecules. Although the research undertaken in gas-phase EMF research is much less widespread compared to those engaged in the synthesis, separation, and application of EMFs, the gas-phase results still provide valuable clues for new members in the family of EMF. On the one hand, these novel EMF species observed in the gas phase provide direct experimental evidence for their existence and valuable clues for their solid-phase synthesis methods, which can promote the exploration and discovery of new synthesis methods for EMFs. On the other hand, the structural study of these new EMF species can provide insights into their novel structures and new chemical bonds, different properties, and potential applications.

Experimentally, high-resolution mass spectrometry is widely applied to qualitatively identify charged EMF species and their molecular compositions. The distributions of EMF ions related to different experimental conditions, precursors, and metal elements can provide valuable information on the mechanism of the generation of important and novel EMF species, especially when combined with theoretical calculations. Among them, the selection of precursors is found to be important, and it is worth noting that, in future research, the synthesis of specific novel EMFs can be more effectively achieved by selecting appropriate precursors. However, it should be pointed out that a great deal of essential work in gas-phase EMF study still needs to be done. First, new methods for the generation of new or novel EMF ions are necessary. Considering that the bottom-up mechanism dominates most laser ablation experiments, based on the Smalley-type source, different generation and ionization methods based on the top-down mechanism are needed for large-size or special EMF ions. Different precursors and new sample preparation methods are important, too. Second, the formation of EMFs encaging transition metals is one of the most fascinating topics in gas-phase EMF chemistry. It is also an important means of discovering novel EMFs. Considering the examples of $\text{La}_2\text{Pt@C}_{90}$, and $\text{La}_3\text{Pt@C}_{98}$, it is natural to assume that more types of embedded metal clusters or ionic bonds can be discovered or synthesized. On the other hand, the ionic bonds composed of different elements can provide new members for the EMF family and may be applied as crucial components of molecular devices. Third, it is expected that more methods of ion chemistry should be applied to the investigation of the structure and characteristics of gas-phase fullerene ions. In addition to the widely used method of CID, other methods, such as reaction mass spectrometry, collisional section measurement, UV photodissociation spectroscopy, etc., should be combined in tandem mass spectrometric study. Fourth, the gas-phase study of EMF anions, which may open up a different path for discovering new EMFs, is still very limited.

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