Short communication

TIMS and MALDI TOF of endohedral $Li_n@C_{70}$ (n = 1 – 3) metallofullerenes

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Using the ion implantation technique (introducing negatively charged fullerene into a low temperature lithium plasma column by a strong axial magnetic field) endohedral fullerenes $Li@C_{70}$, $Li_2@C_{70}$ and $Li_3@C_{70}$ were produced. Mass spectral studies (both TIMS-thermal ionization mass spectrometry and MALDI TOF MS - matrix assisted laser desorption ionization time-of-flight mass spectrometry) of these endohedral fullerenes provided detailed structural and reactivity information about these unusual species. The fragmentation of the obtained ions is shown to be by a multiple C_2 loss (shrink-wrap mechanism). According to the fact that more atoms in the fullerene make the produced endohedral less stable, $Li_3@C_{70}$ shows a big degree of instability. The presence of $Li_3@C_{70}$ was observed on MALDI TOF MS.

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1. Introduction

Endohedral fullerenes, or fullerenes that, thanks to their unusual cage like structure with inner empty space, have trapped atomic or molecular species, have been studied a lot, both experimentally and theoretically. Up to now, there has been made a lot of endohedral fullerenes [1, 2], both by encapsulating non metallic and metallic species in fullerenes. Many metals including group 3 metals (Sc, Y, La), group 2 metals (Be, Ca, Sr, Ba), alkali metals (Li, Na, K, Rb, Cs) and some tetravalent metals have been successfully encapsulated into fullerenes to form metallofullerenes. These new materials are very important for their potential application as new types of superconductors [3], nonlinear optical materials [4], magnetic resonance imaging agents [5], biological tracing agents [6] etc.

As one of the important properties of endohedral fullerenes, which also lead to the proof of their endohedrallity is fragmentation by "shrink wrap" mechanism [7] or multiple C_2 loss. By sequential elimination of C_2 endohedral fullerenes fragment to the smallest stable endohedral cages whose cage sizes are dependent of ionic radii of the encapsulated metal.

By investigating the reactivity of endohedral fullerene molecules in the gas phase it has been concluded that these molecules do not react with molecules such as H_2, O_2, NO, NH_3. This non reactivity points out that the metal atom is trapped and protected inside the fullerene cage. Non reactivity with oxygen rich molecules and fragmentation by "shrink wrap" mechanism are the main proofs of endohedral structure of these molecules.

Endohedral fullerenes can be prepared simultaneously during the fullerene formation, by laser vaporization method [8] or arc discharge method [9], by adding the appropriate material during the formation of fullerenes. Formation of endohedral compounds by ion implantation [10] is the process of encapsulating the atom into the fullerene cage which is already synthesized. This technique has been applied to lithium and other alkali atom fullerenes [11, 12]. Endohedral fullerenes of alkali metal ions $M@C_{60}$ (M = Li, Na, K) [13] are shown to be obtained by collision of metal ion M^+ with C_{60} in gas phase in mass spectrometer. The suggested mechanism of Li encapsulation is "slip through" mechanism. Campbell and coworkers [14] showed that alkali metal endohedral fullerenes can be produced by bombarding C_{60} films on Si substrate with beam of alkali metal ions M^+ (M = Li, Na, K, Rb).

In this work we have studied the formation of lithium endohedral fullerenes $Li_n@C_{70}$ (n = 1, 2, 3) by thermal ionization mass spectrometry, and made characterization of obtained endohedrals by TIMS and MALDI TOF mass spectrometry.

2. Experimental

The experiments of synthesis of lithium endohedral fullerenes were performed on TIMS (Thermal Ionization Mass Spectrometer). It is a 12-inch radius, 90º sector magnetic instrument of local design. The instrument is equipped with few different kinds of ion sources which are placed around the ionization chamber. Surface ionization ion source is placed in the middle of this chamber. Surface ionization, a method used for the production of endohedral fullerenes in this work, is a method of generating ions at a hot metal surface. The sample is placed on a metal filament (Re) and put in the ionization chamber. By heating the filament, part of the sample evaporates as positive or negative ions. We used a triple filament surface ionization ion source, made up of two side filaments (evaporation filaments) and central filament (ionization filament). The sample is placed on the evaporation filaments and evaporated at the appropriate temperature onto much hotter ionization filament on which the beam particles were ionized.

The samples used in this experiment were C_{70} as a generator of C_{70}^- ions and LiI as a generator of Li^+ ions. By introducing negatively charged fullerene into a low temperature lithium plasma column by a strong axial magnetic field (ion implantation technique) endohedral fullerenes $Li@C_{70}$, $Li_2@C_{70}$ and $Li_3@C_{70}$ were produced. These molecules were ionized using the surface ionization technique. Their existence was demonstrated through the high sensitivity mass spectrometer.

After completion of the reaction on TIMS, the obtained powdered material was collected from the cold parts of the ion source for the MALDI TOF mass spectral analysis. MALDI TOF MS (Matrix Assisted Laser Desorption Ionization Time-of-Flight Mass Spectrometer) Voyager de Pro (AB Applied Biosystem, UK) is a commercial mass spectrometer. The sample activation has been achieved applying a nitrogen laser providing ultraviolet light of 337 nm with a pulse width of 3 ns and a pulse frequency of 1,5 Hz. The instrument operates on a continuous acceleration voltage of 20 kV. For MALDI TOF analysis of lithium endohedral fullerenes we used DCTB (2-[(2E)-3-(4-*tert*-butylphennyl)-2-methylprop-2-enylidene] malononitrile) as matrix.

3. Results

Mass spectra of lithium endohedral ions obtained on TIMS are shown in Fig. 1. [15].

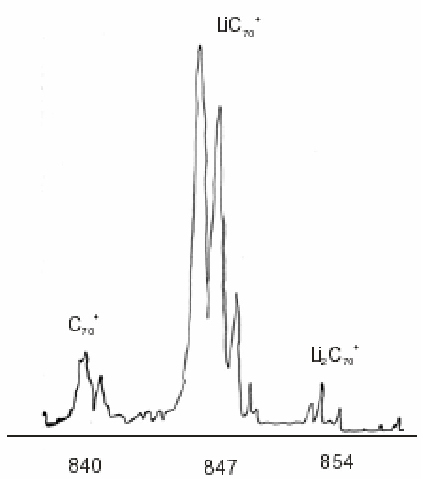

Fig. 1. Mass spectrum of C_{70} / LiI sample containing C_{70}^+, $Li@C_{70}^+$ and $Li_2@C_{70}^+$ [15].

The formation mechanism of Li endohedral fullerenes is via collisions between Li^+ and C_{60}^- in a plasma state. Li^+ ions were formed by surface ionization mechanism from LiI, and C_{60}^- ions were easily obtained by electron impact, since unusually high electron affinity of C_{60}. $Li@C_{70}^+$ and $Li_2@C_{70}^+$ are surface ions, produced by surface ionization of the obtained endohedral fullerenes $Li@C_{70}$ and $Li_2@C_{70}$.

MALDI TOF mass spectral analysis of the powdered material collected from the cold parts of the ion source after completion of the reaction reproduced the results obtained during the *in situ* experiments, figure 2. Beside the signals of $Li@C_{70}$ and $Li_2@C_{70}$ on MALDI TOF mass spectra we can also see the signal of $Li_3@C_{70}$. This signal shows a big degree of instability, which is in accordance with the fact that as more atoms is encapsulated in the fullerene cage the stability of the obtained endohedral molecule decreases. Since the yield of $Li_3@C_{70}$ is very low, it could not be seen by TIMS.

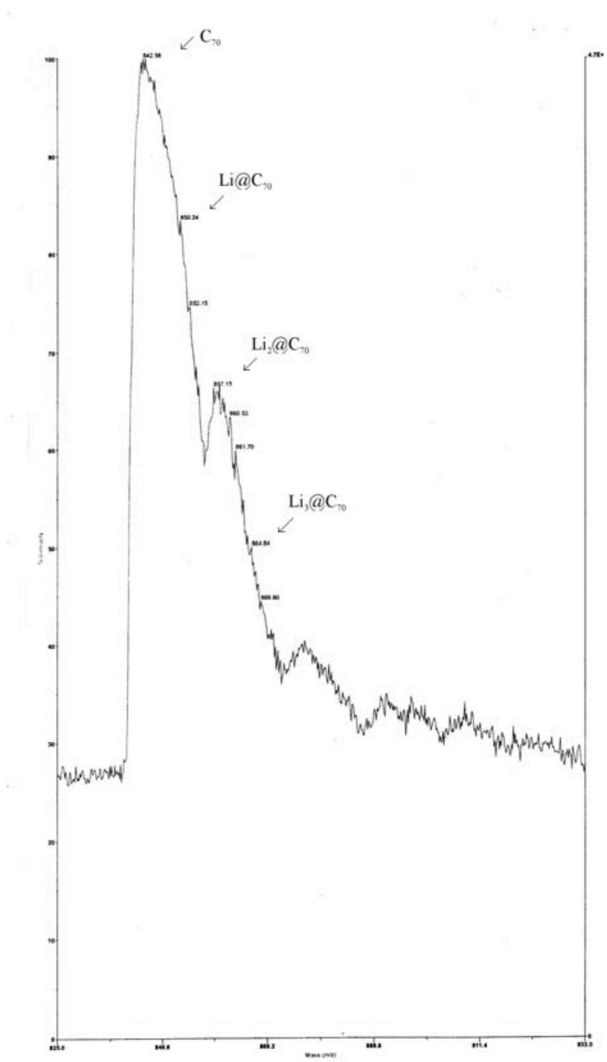

Fig. 2. MALDI TOF mass spectra of C_{70}, $Li@C_{70}$, $Li_2@C_{70}$ and $Li_3@C_{70}$.

The unusual structure of the obtained endohedral fullerenes (where lithium atom is encapsulated in the fullerene cage) was confirmed by two main proofs for endohedrality. Contrary to the exohedral fullerenes, these species shown to be non reactive with the oxygen rich molecules, which was the first evidence of their endohedral structure. As the second evidence, the ions of the obtained endohedral fullerenes were shown to undergo the shrinkwrap mechanism, demonstrated through the loss of C_2 unit from the cage, which is shown in figure 3. It can be seen that multiple C_2 loss in the case of $Li@C_{70}^{++}$ leads to formation of smaller but stable $Li@C_{60}^{++}$.

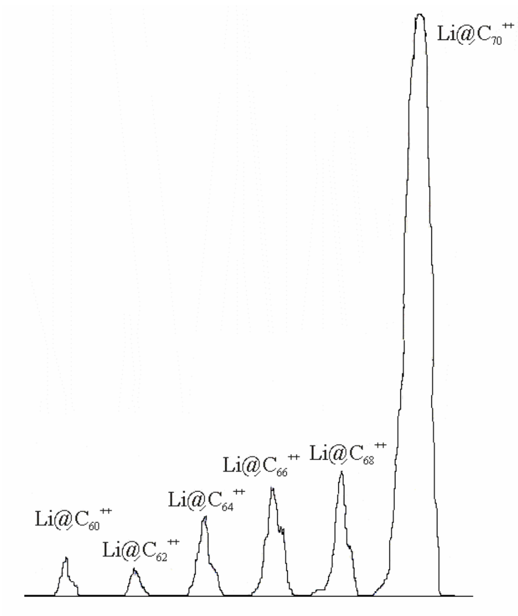

Fig. 3. $Li@C_{70}^{++}$ fragmentation.

4. Conclusion

This work showed that the technique of thermal ionization mass spectrometry can be successfully used for synthesis of lithium endohedral fullerenes, whose existence is proved by multiple C_2 loss fragmentation mechanism. It is also shown that beside encapsulation of one lithium atom in the fullerene cage this technique can be used for encapsulation of two and even three lithium atoms which is shown by MALDI TOF mass spectral analysis. It is also shown that more atoms encapsulated in the fullerene cage makes the obtained endohedral molecule lees stable.

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