

Chapter 2

History of Li@C₆₀

Abstract Whereas endohedral metallo[60]fullerenes with lanthanide and alkaline earth metals were formed by laser vaporization or arc discharge, endohedral alkali metal-containing [60]fullerenes were produced by colliding ion beams or plasma with C₆₀. In experiment colliding a lithium ion beam with C₆₀, a mass peak assignable to Li@C₆₀ was detected. Potassium plasma was also used, and a peak assignable to K@C₆₀ was detected by mass spectrometry. Campbell and co-workers developed ion implantation method based on repeated irradiation of C₆₀ with a lithium ion beam with the aim of isolating Li@C₆₀. After applying this method, Li@C₆₀ was extracted from the deposited film, and a fraction containing predominantly Li@C₆₀ was separated by HPLC. Some physical properties of Li@C₆₀ were investigated. The measured second-harmonic generation response of Li@C₆₀ in the film as well as the third-order susceptibility of Li@C₆₀ suggested that Li in the C₆₀ cage enhances its second hyperpolarizability. The resistivity of the Li@C₆₀ film was measured as 1.5 kΩ cm, about four orders of magnitude smaller than that of C₆₀ films (*ca.* 50 MΩ cm).

Keywords Alkali metals • Lithium ion beam • Lithium plasma • Ion implantation method • Collision energy

2.1 Introduction

Apart from endohedral metallo[60]fullerenes, the general method for producing endohedral metallofullerenes involves heating graphite rods containing a metal source to high temperature by using laser irradiation or an arc discharge [1]. Then, the metal atoms are encapsulated into the fullerene cage during the formation of fullerenes, which affords endohedral metallofullerenes of various sizes. Another approach involves forcibly putting atoms into the fullerene cages that are prepared in advance. This method is usually used to produce endohedral [60]fullerenes

containing noble gases, as described in Chap. 1. Furthermore, researchers have attempted to produce endohedral fullerenes by applying a strong electric field instead of high temperatures since the early stage of fullerene science.

This chapter describes the production, purification, and physical evaluation of alkaline metal-containing [60]fullerenes, in particular Li@C₆₀, prepared by the ion implantation method, which was first reported in the late 1990s to early 2000s. Although some experimental data are inconsistent with those obtained after the recent successful isolation of Li@C₆₀ as a solid (Chap. 7), the materials obtained in this early research undoubtedly involved the Li@C₆₀ structure and provided valuable information for further research on Li@C₆₀.

2.2 Detection of Alkali Metal-Containing C₆₀

Anderson and co-workers performed collision experiments using Li, Na, and K ion beams to collide with fullerenes [2], while collision experiment had previously been attempted using other types of ion beams [3–6]. A mixture of C₆₀ and C₇₀ was vaporized at approximately 340 °C, metal ion beams were irradiated onto the evaporated fullerene mixture, and then the products and unreacted ions were analyzed by mass spectrometry. A molecular ion peak corresponding to the alkali metals plus C₆₀ as well as peaks for species with elimination of C₂ units was observed, and the peak ratio varied as the applied energy of the ion beams was changed. For example, the molecular ion peak for the LiC₆₀⁺ reached a maximum at approximately 20–30 eV, and irradiation with larger energy produced peaks for fragmentation ions such as LiC₅₈⁺ with the loss of a C₂ fragment as well as peaks for C_{60–2n}⁺ ($n = 0, 1, 2, \dots$) with the loss of the lithium atom. The observed mass spectra for ion beam collision energies of 35 and 74 eV are shown in Fig. 2.1. As shown in the figure, there is an optimal metal ion collision energy, above which molecules decompose by fragmentation. The amount of the product obtained by the reaction of ion beams with fullerenes is very small. As in studies of other endohedral fullerenes in early fullerene research, the generation of LiC₆₀ was detected by mass spectrometry only.

Reactions involving treatment of C₆₀ with potassium plasma rather than ion beam irradiation were reported by Hatakeyama, Sato, and co-workers [7]. Potassium plasma, which was generated by surface ionization of K atoms on a hot plate, was reacted directly with the C₆₀ vapor. Mass spectra of the obtained thin films exhibited a peak assigned to KC₆₀. They surmised that electrons in the plasma reacted with C₆₀ to generate C₆₀[−], creating a potassium–fullerene plasma that reacted with K⁺ to produce K@C₆₀. Although this process produced only a small amount of endohedral metallo[60]fullerenes, the plasma method became the basis for manufacturing an apparatus for Li@C₆₀ production.

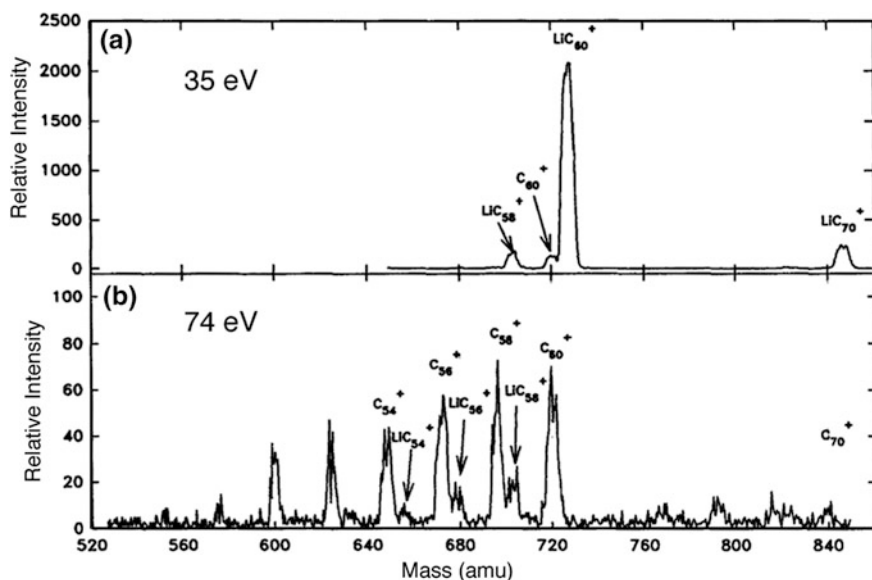


Fig. 2.1 Mass spectra of $\text{Li}^+ + \text{C}_{60}$ at collision energies of **a** 35 eV and **b** 74 eV. Reprinted with permission from Ref. [2]. Copyright (1993) American Institute of Physics

2.3 Ion Implantation Method and Purification

With further improvement of Anderson's ion collision method, Campbell and co-workers conducted scale-up experiments using a deposited C_{60} films and ion beams and reported the synthesis of endohedral metallo[60]fullerenes in sufficient quantities for handling in 1996 [8]. Figure 2.2 shows their vacuum deposition apparatus for production of endohedral metallo[60]fullerenes [9]. The vapor-deposited C_{60} film on a substrate shown on the right-hand side of the figure is transferred to the left-hand side and irradiated with a Li^+ ion beam with its collision energy controlled by an applied bias voltage. The substrate is transferred back to the right-hand side, and C_{60} is vapor-deposited again over the existing film. They reported that alternating deposition of C_{60} thin films and exposure to the Li^+ ion beam produced 15–20 μg of $\text{Li}@\text{C}_{60}$ per hour. The amount of $\text{Li}@\text{C}_{60}$ was estimated by laser desorption ionization time-of-flight (LDI-TOF) mass spectrometry (Fig. 2.3a). A peak at $m/z = 727$ to the right of the C_{60} peak ($m/z = 720$) was assigned to $\text{Li}@\text{C}_{60}$. This mass spectrum was obtained for a sample prepared with a collision energy of 30 eV and a 6:1 molar ratio of irradiated Li to deposited C_{60} . The amount of $\text{Li}@\text{C}_{60}$ obtained was significantly influenced by the energy of the Li^+ ion beam. Figure 2.3b shows a plot for the ratio of produced $\text{Li}@\text{C}_{60}$ to C_{60} , as

Fig. 2.2 Schematic illustration of the experimental setup for production of Li@C_{60} . Reprinted with permission from Ref. [9]. Copyright (1997) Elsevier B.V

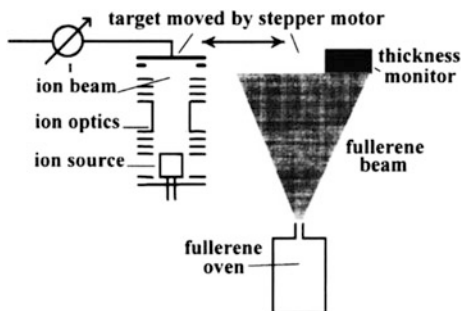
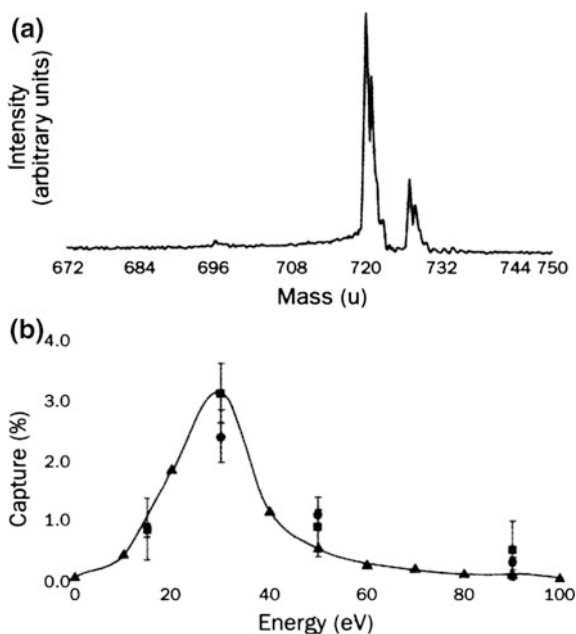


Fig. 2.3 **a** Mass spectrum of a C_{60} film irradiated with a Li^+ ion beam. **b** Plot of the ratio of produced Li@C_{60} to C_{60} versus Li^+ ion beam energy. Reprinted with permission from Ref. [8]. Copyright (1996) Nature Publishing Group



obtained from the ratio of molecular ion peaks for Li@C_{60} to C_{60} , versus irradiated beam energy. The production of Li@C_{60} was found to reach a maximum around 30 eV.

Using the repeated ion beam irradiation method, Campbell and co-workers enthusiastically produced Li@C_{60} . In the following year, 1997, they reported the extraction of Li@C_{60} from the deposited films with carbon disulfide and the purification of Li@C_{60} by HPLC [10]. During the HPLC separation, they used also carbon disulfide as the mobile phase with a Buckyprep or 5PBB (pentabromobenzyl) column (Nacalai Tesque), both of which are well known for fullerenes purification. Figure 2.4a shows an HPLC profile when the 5PBB column was used.

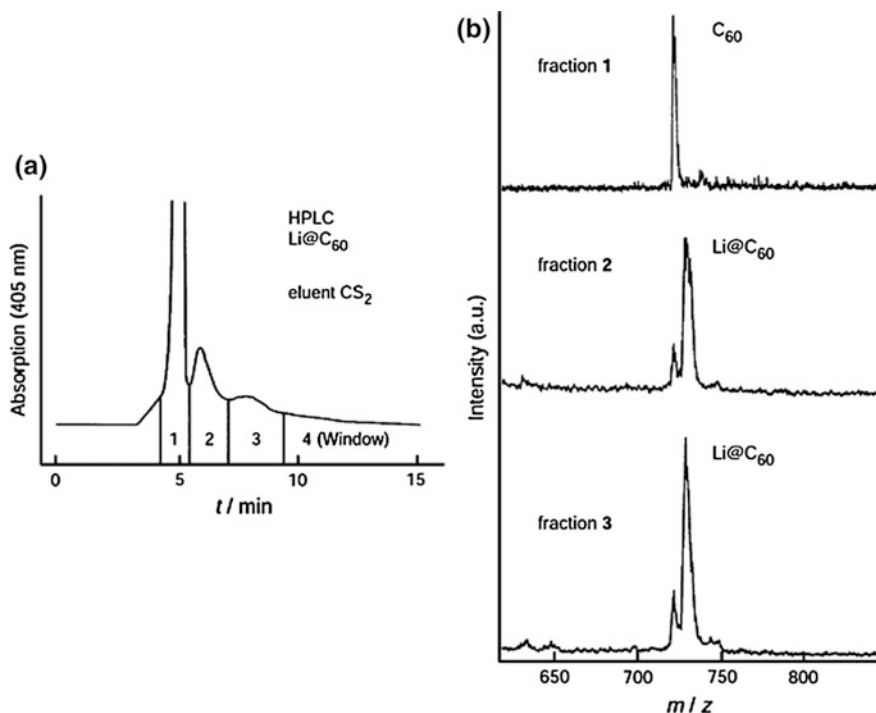


Fig. 2.4 **a** HPLC profile of the CS₂ extract of thin films containing Li@C₆₀. **b** LDI-TOF mass spectra for the *fractions 1, 2, and 3*. Reprinted with permission from Ref. [10]. Copyright (1997) Royal Society of Chemistry

Mass spectra for fractions 1, 2, and 3 are shown in Fig. 2.4b. A fraction containing Li@C₆₀ eluted after elution of C₆₀. They also reported thin films showing good solubility in carbon disulfide. As mentioned above, optimal molar ratio of Li⁺ to C₆₀ was 6:1 for the formation of Li@C₆₀ as judged from mass spectra for deposited thin films. However, they found that the thin film prepared with a Li⁺:C₆₀ ratio of 1:1 showed better solubility than the one prepared with a 6:1 ratio. With a condition of the 1:1 materials ratio, the amount of empty C₆₀ in the deposited film is increased, but they found this condition is more efficient for production of Li@C₆₀ with the higher solubility of deposited films.

Campbell and co-workers then sought to characterize the purified Li@C₆₀. In 2003, they reported IR and Raman spectra of eluents containing Li@C₆₀ fractionated by HPLC [11]. These spectra were intricate and showed numerous peaks. They hypothesized the existence of dimer and trimer structures with C₆₀ cages bonding to the Li@C₆₀ component based on their spectroscopic data and previous reports describing the behavior of Li@C₆₀.

2.4 Properties of Li@C₆₀ in Early Research

Although the amount of Li@C₆₀ obtained by the Campbell's method was not large by today's standards, the necessary amount for evaluation could be prepared by repeatedly applying their method. With several milligrams of materials in hand, they evaluated various physical properties of Li@C₆₀. They measured thermal properties including thermal desorption spectroscopy [12] and thermal stability [13]. In addition, they observed thermal elimination of Li@C₆₀ and Li₂@C₆₀ molecules from films prepared by low-energy ion bombardment of C₆₀. The binding energy between fullerenes was increased by lithium ion beam irradiation. In other words, this treatment made elimination of C₆₀ from the film difficult. Li@C₆₀ was found to be less thermally stable in solution (e.g., fractions 2 and 3 in Fig. 2.4a) than in the solid state. It would gradually decompose in solution accompanied by elimination of Li and dimerization.

In 1998, large hyperpolarizability of Li@C₆₀ was estimated in theoretical studies, and the second-harmonic generation (SHG) response of Li@C₆₀ within the film was reported [14]. In 1999, the third-order susceptibility of Li@C₆₀ was also reported [15]. These data suggested that the Li atom in the C₆₀ cage enhances its second hyperpolarizability.

Electrical measurements of Li@C₆₀ were also performed [16]. A sample purified by HPLC (as described in the Sect. 2.3) was vapor-deposited on silicon substrates and subjected to resistivity measurement, showing a resistivity value of 1.5 kΩ cm, several orders of magnitude less than that of C₆₀ films (*ca.* 50 MΩ cm). This observation suggests that charge transfer from the encapsulated Li atom to the fullerene cage increases conductance. This resistivity value for the Li@C₆₀ films was measured under high vacuum, but increased to 4 MΩ cm upon exposure to air for 2 min and to a value comparable with that of C₆₀ films upon exposure to air for 1 h. The measurement configuration and *I*–*V* characteristics are shown in Figs. 2.5 and 2.6, respectively.

Electron paramagnetic resonance (EPR) was measured for Li@C₆₀, and a small signal was observed at $g = 2.0025 \pm 0.0005$ [16]. A similar signal was also observed for the C₆₀ solid. In the case of C₆₀, this signal is assigned to a very small amount of C₆₀⁺ present. This observation implies that valence electrons originating from the Li atom contribute to bonding between fullerene cages. The electron spin–lattice relaxation time was different between Li@C₆₀ and C₆₀, presumably because of the symmetry reduction caused by encapsulation of the Li atom in the fullerene cage.

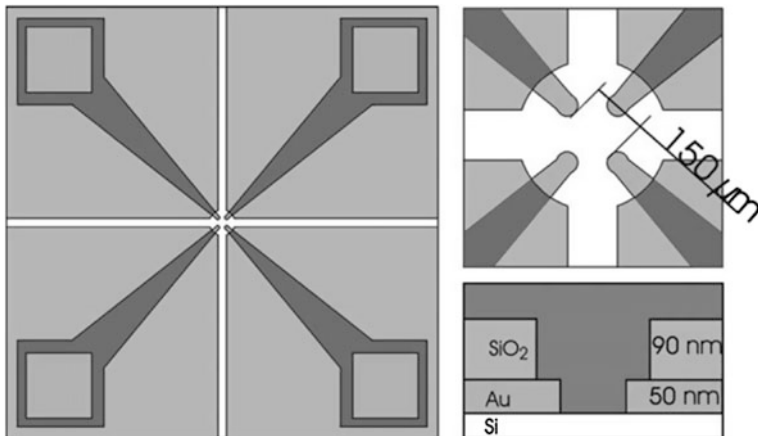


Fig. 2.5 Configuration for resistivity measurements. Reprinted with permission from Ref. [16]. Copyright (2005) Elsevier B.V

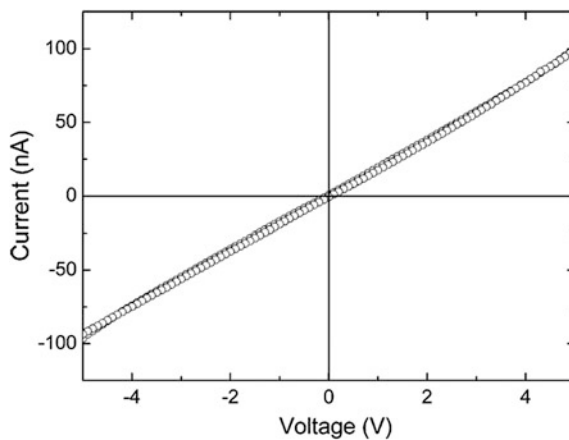


Fig. 2.6 I - V dependences for Li@C_{60} films measured under high vacuum. Reprinted with permission from Ref. [16]. Copyright (2005) Elsevier B.V

2.5 Conclusion

Li@C_{60} was produced by Li^+ ion beam irradiation onto vapor-deposited C_{60} . Some studies investigated the physical properties of isolated Li@C_{60} . However, in absolute terms, the amount of material that could be prepared by this production method was still small for full chemical and structural characterization, including NMR measurements, elemental analysis, and X-ray crystallography. The existence of Li@C_{60} was confirmed by only mass spectrometry. To account for the difficulty

of characterization, researchers considered the possibility of dimer or trimer formation. In 2016, full chemical and structural characterization of endohedral lithium-containing [60]fullerene was, at long last, achieved through isolation and purification of lithium-ion-containing [60]fullerene (Li⁺@C₆₀), followed by its reduction to neutral lithium-containing [60]fullerene (Li@C₆₀) [17].

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