

Preface

Fullerenes and fullerene derivatives have been studied in pure science since C_{60} was discovered in 1985, and are currently used in energy and biology related materials fields. Recently, endohedral lithium-containing [60] fullerenes, emerging fullerene-based materials, have attracted extensive attention because of their exotic properties such as their remarkable electron affinity, extraordinary chemical reactivity, and unique energy absorption properties. These properties are derived from an inner Li^+ ion or Li atom inside a C_{60} cage. The endohedral lithium-containing [60]fullerenes involve Li^+ -containing C_{60} , $Li^+@C_{60}$ and Li-containing C_{60} , $Li@C_{60}$. Initially, scientists tried to produce $Li@C_{60}$ by means of lithium ion beams or lithium plasma through collisions between Li^+ and C_{60} . This effort led to the successful formation of $Li@C_{60}$. However, they faced difficulty with the separation and purification of $Li@C_{60}$. Although purification of $Li@C_{60}$ was partially achieved, complete purification to a satisfactory level for full chemical characterization was found to be difficult because of unfavorable charge transfer interactions between $Li@C_{60}$ and empty C_{60} . Faced with this tough challenge, scientists solved the problem by the chemical oxidation of $Li@C_{60}$ into $Li^+@C_{60}$ to suppress this interaction. At length, $Li^+@C_{60}$ was isolated in pure form using a chromatographic technique, and then fully characterized through various spectroscopic studies such as nuclear magnetic resonance, mass spectroscopy, and electrochemical measurements. Furthermore, $Li^+@C_{60}$ salts with counter anions such as PF_6^- and $SbCl_6^-$ were structurally characterized by synchrotron radiation X-ray crystallographic studies. This structural determination unambiguously proved encapsulation of Li^+ inside a C_{60} cage. Following on from this, scientists immediately started chemical research using isolated $Li^+@C_{60}$. Initially, scientists demonstrated the synthesis of a PCBM-type $Li^+@C_{60}$ derivative although this required significant effort. Syntheses of Diels–Alder adducts, fullereneols, organometallic complexes, and supramolecular complexes were also achieved by utilizing the strong electron-accepting nature of $Li^+@C_{60}$. Additionally, by using $Li^+@C_{60}$ as unique ionic electron acceptors, photo-induced electron transfer using various cationic electron donors was investigated in detail. Long-lived charge separated states were precisely elucidated and applied to a photovoltaic system. Furthermore, the electrochemical synthesis of

neutral Li@C_{60} was also achieved utilizing an ionic conductive property of $\text{Li}^+\text{@C}_{60}$ as an electrolyte in solution. Electrolysis of $\text{Li}^+\text{@C}_{60}$ without using any other electrolyte successfully produced Li@C_{60} on an electrode. Spectroscopic studies and X-ray crystallographic analysis revealed that Li@C_{60} is in a charge-separated form expressed formally as $\text{Li}^+\text{@C}_{60}^{\bullet-}$. It can be regarded as a model of a super-atom, particularly the hydrogen atom having a central nucleus and a surrounding electron orbital. Many theoretical studies were performed to elucidate formation mechanisms, electronic structures, physical properties, and chemical reactivities of Li@C_{60} and $\text{Li}^+\text{@C}_{60}$. Research of Li@C_{60} and $\text{Li}^+\text{@C}_{60}$ is now widely expanding to interdisciplinary areas for example physical measurement techniques such as photoemission, dielectric properties, and terahertz absorption measurements as well as transmission electron microscopy observation.

This book comprises nine chapters, covering the history of endohedral lithium-containing [60]fullerenes to their recent synthetic and application studies. The contents straddle interdisciplinary areas of chemistry and physics. Application of these materials in biological fields is also expected in future research. The wide-ranging topics in this book, from organic synthesis to physics, will stimulate interest and widen viewpoints across the research fields of Li@C_{60} and $\text{Li}^+\text{@C}_{60}$.

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