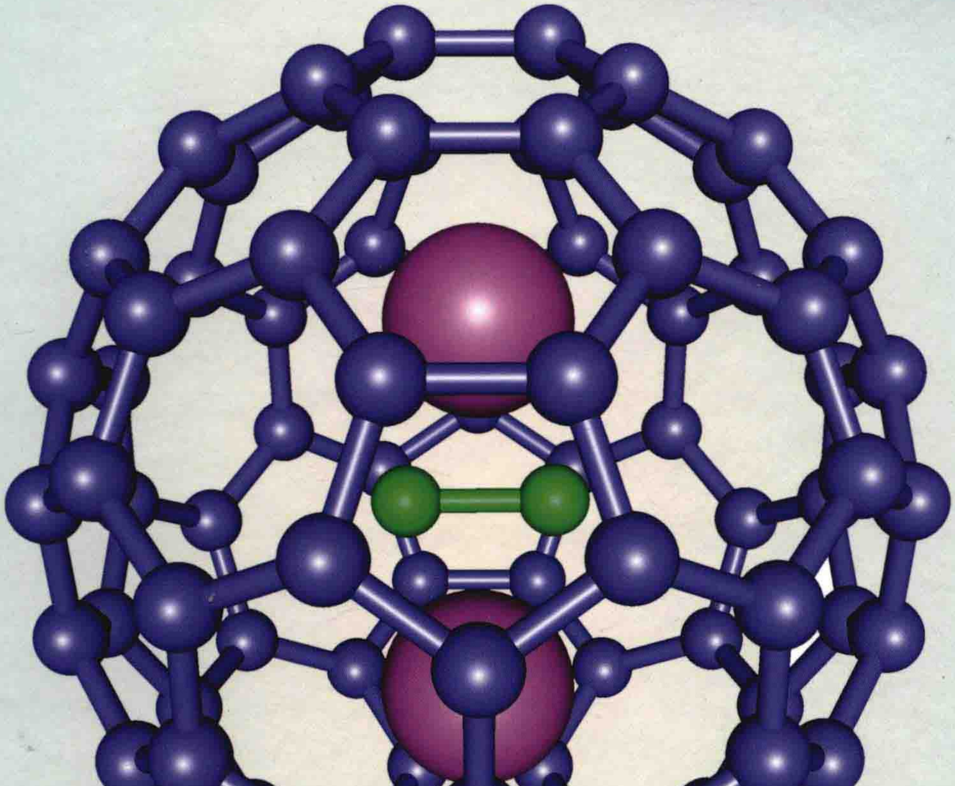
ENDOHEDRAL METALLOFULLERENES

FULLERENES WITH METAL INSIDE

Hisanori Shinohara
Nikos Tagmatarchis



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FULLERENES WITH METAL INSIDE

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Foreword by Sir Harold Kroto

Endohedral metallofullerenes are a fascinating class of fullerene materials because many of the structural, electronic and magnetic properties of the fullerenes change drastically upon encapsulation of metal atoms. Consequently these materials offer practical applications in a variety of areas including solar cells and biomedicine.

Endohedral Metallofullerenes: Fullerenes with Metal Inside presents a comprehensive survey of the current state of knowledge on endohedral metallofullerenes, from preparation to functionalization, reactivity and applications. Following a brief historical overview, the book describes methods for synthesis, extraction, separation and purification, and provides an insight into the molecular and crystal structures. Subsequent chapters discuss various categories of endohedral metallofullerenes based on the encapsulated species, including carbides, nitrides, sulphides, oxides, non-metal and non-IPR endohedral metallofullerenes, followed by scanning tunneling microscopy studies and the examination of electronic, vibrational, magnetic and optical properties. The book concludes with chapters addressing the chemical functionalization of endohedral metallofullerenes, and applications ranging from solar cells to biomedicine.

This book will provide scientists, researchers and students in the field of nanocarbons and nanomaterials with a fresh and authoritative look at the diverse areas of endohedral metallofullerenes.

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Also available as an e-book

ISBN 978-1-119-94272-6

9 781119 942726

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This edition first published 2015

Registered Office
John Wiley & Sons, Ltd., The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ, United Kingdom

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Library of Congress Cataloging-in-Publication data applied for.

ISBN: 9781119942726

A catalogue record for this book is available from the British Library.

Set in 10.5/13pt Sabon by SPi Global, Pondicherry, India

Printed and bound in Singapore by Markono Print Media Pte Ltd

1 2015

Endohedral Metallofullerenes

Foreword

At the end of the hectic couple of weeks in 1985 during which C_{60} Buckminsterfullerene was discovered, as I was leaving Houston I suggested to Sean O'Brien (one of the wonderful group of students involved in the discovery) that if the molecule really was a fullerene cage it should be possible to put an atom inside it. I suggested on the basis of my familiarity with ferrocene that an iron atom might be a good bet. Unfortunately that was not a good choice as Sean could not get a mass spectrometric signal for such a species. The next day Jim Heath tried lanthanum which went in successfully and led to the second fullerene paper on La@C_{60}. I am not sure that Sean ever forgave me for suggesting iron and indeed I think that to this day no iron-containing fullerene has been discovered, which is actually rather interesting. During the period after the discovery, I discovered the fact that a small fullerene tetrahedral C_{28} should be metastable and perhaps further stabilized by adding four hydrogen atoms, one to each of the four carbon atoms at the tetrahedral apexes. I suggested it might be a sort of tetravalent carbon cluster "superatom." Later on, this tetravalent hypothesis was supported by the Rice group's detection of a metastable endohedral cluster U@C_{28} in which the tetravalency was interestingly satisfied from within by the tetravalent uranium atom. Thus was the amazing novel field of endohedral fullerene chemistry born. I do not think that for one second we ever imagined that these experiments would result in such an exciting and wide-ranging field of unique chemistry which this compendium beautifully highlights.

Harold Kroto
Tallahassee, USA
January 2015

Preface

Since the first experimental discovery of C_{60} fullerene by Kroto, Smalley and co-workers in 1985, the term nanocarbons or carbon nanomaterials (including carbon nanotubes and graphene) has been emerged and prevailed quite rapidly in the area of nanoscience and nanotechnology as well as of materials science in general. One of the crucial factors of this prevalence is the discovery of macroscopic synthesis of fullerenes by Kräetschmer, Huffman and co-workers in 1990.

In fact, during the past decade, fullerenes have already been practically applied as important constituents of various composite materials such as solar cells, reinforcing materials for sporting goods, lubricants of car engine oils and even cosmetics. In particular, practical applications of certain functionalized fullerenes as a brand-new solar cell battery have been a competitive and heated R&D target in chemical and electric industrial companies worldwide. Unlike the conventional silicon-based solar cells, solution-based fullerene solar cells possess unique and novel characteristics of paintable and flexible performance.

One of the most intriguing outgrowths of fullerenes is the so-called "endohedral metallofullerenes", fullerenes with metal(s) encapsulated. One may easily think that the metallofullerenes might exhibit salient electronic and magnetic properties which are totally different from those of the conventional (empty) fullerenes: the presence of a atom even within a fullerene may drastically alter its electronic properties. The origin of the metallofullerene can be traced back to 1985, a week after C_{60} was experimentally discovered by the Sussex-Rice research team. Their idea is quite simple: if C_{60} has a spherical hollow shape as the first Nature paper advocates, then C_{60} can encage a metal atom inside. Indeed, in their second paper, they performed laser-vaporization cluster-beam time-of-flight mass spectrometry using lanthanum-doped graphite disks and observed an enhanced peak due to La@C_{60} in a mass spectrum, suggesting that the La atom is safely entrapped inside C_{60} as expected.

Up until early 1990's, however, there had been a heated and controversial discussion as to whether or not a metal atom is really entrapped inside of the fullerene or rather externally bound from outside. The first experimental verification of the endohedral nature was brought by the Nagoya-Mie research team in 1995 when they performed synchrotron X-ray powder diffraction on a chromatographically purified metallofullerene sample.

Now that the existence of "endohedral metallofullerenes" had been confirmed, there was an outbreak of research in the area of this brand-new fullerene family. This book primarily deals with the research and development of the metallofullerene after 1995, where synthesis, purification, structures, electronic/magnetic properties and some of the important applications of different types of metallofullerenes are fully and chronologically described.

The authors acknowledge fruitful collaborations and discussion with a number of our present and former graduate students, postdocs and laboratory research staff. We must apologize for not mentioning them individually. We also thank our publishers for their encouragement and patience. Last but, of course, never least, we want to thank our families for their continuing support.

Hisanori Shinohara, Nagoya
Nikos Tagmatarchis, Athens
April 2015

Personal Reflection – Nori Shinohara

At the breakfast table at a small hotel on the shore of Lake Konstanz in Germany, Rick Smalley, who was a professor at Rice University at the time, showed me a slide for a presentation. It was Wednesday, September 12, 1990. He asked, "Nori (my nickname), do you know what the fine black powder at the lower right of this slide is?" It was C_{60} powder! I was momentarily stunned by what I saw on the slide that Smalley handed me and could not immediately understand what had happened [1].

Smalley and I were by chance staying at the same hotel while attending the 5th International Symposium on Small Particles and Inorganic Clusters (ISSPIC 5) (Figure 1) that was being held at the University of Konstanz in Germany, September 10–14, 1990. The organizers were the cluster physicists Eckehalt Recknagel (a University of Konstanz professor at the time) and Olof Echt (a University of New Hampshire professor).

The first announcement of the easy and astonishing macroscopic synthesis of C_{60} by sublimation of graphite was made at this symposium, which is well-known in the fields of clusters and ultra-fine particles. Furthermore, the announcement of the century concerning macroscopic synthesis of fullerenes by Wolfgang Krätschmer was an unannounced presentation that took less than 10 min if I remember correctly. I was also attending the symposium for a presentation of my own research on laser spectroscopy of benzene molecular clusters.

It was a coincidence that Smalley, who would later receive the Nobel Prize for the discovery of fullerenes in 1996 with Harry Kroto and Bob Curl, was also staying with his wife at the small and stylish hotel at which I was staying, the Villa Hotel Barleben am See in Konstanz, the location of the University of Konstanz where the symposium was held.

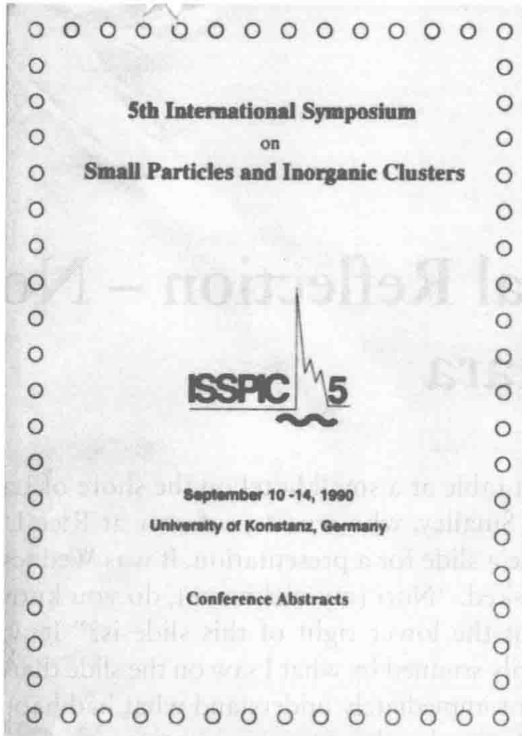

Figure 1 Abstract for ISSPIC 5 held at the University of Konstanz, Germany, September 10–14, 1990

It was the middle day of the conference, September 12. "Solid C_{60} Isolated" was written on Smalley's slide displaying the C_{60} powder.

Fullerenes are the third allotrope of carbon after graphite and diamond, and C_{60} is the most typical molecule among them. In 1985, Rick Smalley, Harry Kroto, and co-workers discovered C_{60} (by chance) using laser-vaporization cluster-beam mass spectroscopy [2], but no one had succeeded at macroscopic synthesis at the time.

Smalley had planned to talk about metal and semiconductor clusters, the research into which he was putting his energy at the time under the title of "ICR Probes of Cluster Surface Chemistry" at this international symposium. However, when Smalley went up to the podium, he abruptly announced that he would talk about C_{60} rather than cluster surface chemistry.

Smalley started this talk with "The first discovery of C_{60} five years ago in 1985 was through joint research between Rice University and the University of Sussex. However, Dr Krätschmer *et al.* of the Max Planck Institute, Heidelberg, have very recently discovered a very simple method for producing large amounts of C_{60}." Smalley abandoned the 50 min lecture he was invited to give and hurriedly had Krätschmer give an unannounced presentation on this important discovery.

According to the discovery by Krätschmer and co-workers [3], C_{60} could easily be produced in large quantities using arc discharge (at this point, more precisely, resistive heating) on graphite. All of the researchers at the symposium were surprised at this. Furthermore, this unannounced presentation was the beginning of all the subsequent research into nanocarbons (e.g., fullerenes, carbon nanotubes, nanopeapods, graphene, etc.), as well as full-scale research on nanotechnology.

After Krätschmer's presentation, most of those attending the symposium returned home to carry out additional testing. From that day forward, there was an explosion of research groups at hundreds of locations worldwide enthusiastically plunging into C_{60} research. This 10 min, unannounced presentation proclaimed the start of global research into fullerenes, carbon nanotubes and, after that, nanocarbons. This was the biggest discovery in the last 50 years, maybe even the discovery of the century, and brought with it a completely new trend in materials science and technology.

That summer I was 36, and my own research also underwent a big change.

As soon as research on fullerenes was ignited, there was the abnormal situation of 30 or more related papers appearing in a single day. Because of this, researchers were driven by a sense of fear, and there was no rest for the weary. There was a sense that the work being done today would be overshadowed the next morning. In fact, though it is only half true and I am half joking, we said that the researchers with the dark circles under their eyes at international conferences were the ones working on fullerenes at the time. It was an absurd period for me, doing things such as staying overnight with students at the laboratory.

I realized that in the midst of this madness, however, many experiments I conducted and reports I wrote would probably be completely forgotten in 4–5 years' time. Therefore, I narrowed down my target to fullerene research and began joint research with Yahachi Saito (currently a Nagoya University professor) on endohedral metallofullerenes, where a metal is inserted into a fullerene cage [1,4,5].

The reason I selected metallofullerenes was that my research on water clusters prior to my research on fullerenes provided important hints for this research. Since water molecules create box-like cage clusters similar to fullerenes [6,7], a molecule or atom can be inserted into the central interior hollow space. Likewise, I thought that it might be possible to encapsulate a metal atom inside a carbon cage. I wondered if I could create a fullerene with completely new electronic and magnetic properties not found up to that time if a metal atom could be placed in this space, since the space in fullerenes is a complete vacuum.

My first report on metallofullerenes [4] was beaten out by Smalley's group, but this research went very well, and it turned out that my joint research with Saito advanced to be top in this field worldwide. In 1995, with the cooperation of Makoto Sakata (a Nagoya University professor at the time) and Masaki Takata [currently a Tohoku University professor], I obtained the first experimental proof of the encapsulation of metal atoms through synchrotron X-ray diffraction measurements (cf. Section 3.2.1).

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 fullerenes.

In the late summer of 1990, I was stunned by the unannounced lecture on macroscopic synthesis of C_{60} by Krätschmer at an international symposium in Konstanz, Germany, and thereafter plunged myself into nanocarbon research. Subsequently, my odyssey of a quarter century in nanocarbon research has taken me into fullerenes, metallofullerenes, carbon nanotubes, peapods and, recently, graphene-related materials. Virtually all of the topics on endohedral metallofullerenes described in this book started after the Konstanz Symposium.

I wonder what novel nanocarbon materials will appear next.

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