Preface

Over the last two decades, the research of endohedral fullerenes has made a dramatic progress. Many types of endohedral fullerenes have been discovered, their production and separation techniques have been substantially improved, and comprehensive studies of their chemical and physical properties became possible. Encapsulation into the interior space of the fullerene cage stabilizes unique metal clusters or single atoms which are not known to exist in the free form. However, this stabilization is only partially achieved by the shielding of the species from the surrounding. Another important factor is that the carbon cage is not "innocent". Namely, the electron transfer between the encapsulated species and the carbon cage plays crucial role in the structure and properties of endohedral metallofullerenes.

Unprecedented molecular and electronic structure of endohedral fullerenes leads to a plethora of phenomena at the interface between the endohedral atoms and π-system of the carbon cage. Charge transfer in endohedral metallofullerene (EMF) molecules can either leave encapsulated species intact (i.e., only carbon cage is active as in empty fullerene) or proceed across the metal–cage interface, and examples of both types are well documented nowadays. The latter case is especially interesting since it opens the way to tune charge states of endohedral species while keeping a fullerene as a protecting shell around the redox center. Good electron accepting properties of fullerenes made them attractive building blocks for organic electronics, and multiple studies of the EMF performance in this role have been carried out, from fundamental photophysical studies of the donor–acceptor dyads to the studies of the photoconversion efficiency in prototype bulk heterojunction solar cells. High thermal stability of endohedral metallofullerenes allows deposition of the molecules on various substrates in ultrahigh vacuum conditions and investigation of their electronic properties with high-resolution scanning probe and other surface science methods. Peculiar electronic states and dynamics of fullerene molecules and endohedral clusters could be investigated with the help of scanning tunneling microscopy.

Single-electron transfer is inevitably accompanied by the change of the spin state of the molecule, and here is another unique property of EMFs: the cage can either keep an unpaired spin itself, or it can transfer the spin to the endohedral cluster, and

hence both the cage and the cluster spin states can be altered. Furthermore, encapsulation of the species with unpaired electrons (e.g., nitrogen or phosphorus atoms or lanthanide-containing clusters) brings endohedral fullerenes to the fields of molecular magnetism and quantum computing. Electron spin resonance, nuclear magnetic resonance, magnetometry, and X-ray magnetic circular dichroism have been used extensively to analyze spin-related phenomena in endohedral fullerenes. Finally, well-defined spin state and long spin coherence make endohedral fullerenes with nitrogen atom, such as $N@C_{60}$, attractive for the field of quantum computing.

The aim of this book is a concise analysis of the behavior of the interface between encapsulated atoms and a carbon-based π-system under conditions of the electron transfer and description of the spin-based phenomena caused by the shielding of endohedral spins by the fullerene cage. In Chap. 1 we introduce the reader into the world of endohedral fullerenes by describing the basics of their synthesis, separation, and molecular structure elucidation. Chapter 2 gives an overview of electrochemical studies of EMFs supported by the molecular orbital analysis. Chapter 3 by Samoylova and Stevenson describes the development in the non-chromatographic separation techniques, which benefit from the difference of reduction and oxidation potentials of different types of EMFs and empty fullerenes. Chapter 4 by Boltalina reviews the studies of the ions of EMFs in the gas phase by various types of mass spectrometry and focuses on the ion molecular reactivity and determination of the electron affinities. In Chap. 5, Zhen, Liu, and Yang give an account on the photoexcitation behavior of EMF in molecular and supramolecular dyads with donors and acceptors and describe possible applications of EMFs in photovoltaics. Chapter 6 by Feng and Petek reviews the studies of the EMFs by low-temperature scanning tunneling microscopy with a focus on superatom electronic state and switching of the molecular geometry by tunneling currents. Chapters 7–9 are devoted to the studies of EMFs by electron spin resonance spectroscopy (ESR). In Chap. 7, Wang and Wang describe ESR studies of Sc and Y-based EMFs. Chapter 8 by Kato reviews ESR spectroscopy of lanthanide EMFs, including those with large spin moments exceeding 1/2. In Chap. 9, we describe EPR studies of ion radicals of EMFs in solution. Magnetic properties of EMFs with endohedral lanthanides are described in Chaps. 10 and 11. Chapter 10 reviews the studies by paramagnetic NMR in solution and describes the use of pNMR for the analysis of molecular structure and dynamics of EMFs as well as for the analysis of the magnetic anisotropy of lanthanide ions in nitride clusterfullerenes. Chapter 11 by Westerström and Greber provides extended introduction into the magnetism of EMF and in particular into single-molecule magnetism of EMFs in bulk and in molecular layers on surfaces. In Chap. 12, Lawler reviews nonmetal endohedral fullerenes with emphasis on dihydrogen-containing fullerenes, their molecular dynamics, and nuclear spin chemistry. Chapter 13 by Zhou and Porfyrakis gives a detailed account of the synthesis and separation of C_{60} with nitrogen atom in its center, $N@C_{60}$, its studies by ESR spectroscopy, and chemical derivatization for the use in quantum computing. In Chap. 14, Harneit describes general concepts of quantum information processing and shows how pnictide endohedral fullerenes, and especially $N@C_{60}$, can be used in this field. We hope that this collection of

chapters prepared by the scientists with diverse expertise and summarizing the vast development of our understanding of the charge transfer and spin-related properties of endohedral fullerenes will bring the information about the fascinating properties of these molecules to the broader audience and inspire further progress in this field.

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