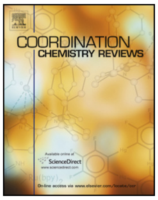
Coordination Chemistry Reviews 257 (2013) 2880–2898

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr



Review

Endohedral metallofullerenes: An unconventional core–shell coordination union

Hailin Cong[a], Bing Yu[a], Takeshi Akasaka[b], Xing Lu[b,*]

[a] *Laboratory for New Fiber Materials and Modern Textile, Growing Base for State Key Laboratory, College of Chemical and Environmental Engineering, Qingdao University, Qingdao 266071, China*

[b] *State Key Laboratory of Materials Processing and Die & Mould Technology, School of Material Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, China*

Contents

---

* Corresponding author. Tel.: +86 2787559404; fax: +86 2787559404.

E-mail addresses: hailincong@yahoo.com (H. Cong), lux@hust.edu.cn, luxing1975@yahoo.com (X. Lu).

http://dx.doi.org/10.1016/j.ccr.2013.05.020

ARTICLE INFO

Article history:
Received 20 March 2013
Accepted 29 May 2013
Available online 13 June 2013

Keywords:
Fullerenes
Metallofullerenes
Metal–cage interaction
Electrochemistry
Spectroscopy

ABSTRACT

Endohedral metallofullerenes (EMFs) are a novel class of metal–carbon hybrid molecules consisting of a fullerene shell and a metal core. Because of the presence of the internal metallic species and charge transfer from metal to cage, EMFs have unique structures and many fascinating properties, which are distinctly different from those of empty fullerenes. The research on EMFs has surprisingly blossomed during recent years, and many practical materials based on EMFs with potential applications in biomedicine, materials science and photovoltaics have been proposed. In this review, we give a systematic and comprehensive summary of the main aspects of EMFs, with emphasis given to experimental results relative to computational work. Finally, perspectives for the future development of EMFs are proposed.

1. Introduction

Fullerenes have a spherical empty space inside the carbon cage, and the interior space of fullerenes can act as a host for a variety of atoms, clusters and molecules to form endofullerenes [1]. Different methods have been developed to generate the core–shell unions encapsulating various species. For example, such readily available molecules as H_2, NH_3, and H_2O can be inserted inside the fullerene cage with the so-called 'fullerene-surgery method', forming unique systems for studying the behavior of isolated molecules [2–4]. In these cases, no obvious communication between the internal elements and the fullerene cage could be observed [5,6]. However, when putting metal atoms or metallic clusters into a fullerene shell, the metal atoms interact strongly with the fullerene cage via electron transfer, and therefore make the resulting core–shell coordination unions unique [7]. This new family of metal–carbon hybrid molecules is commonly called endohedral metallofullerenes (EMFs) [8]. The first example of EMFs, La@C_{60}, was reported by Smalley and coworkers in 1985 soon after their discovery of the famous C_{60} [9]; the first macroscopic synthesis of EMFs was achieved by the same group in 1991 using a laser ablation method and the EMFs were solvent extracted [10]. Thereafter, EMFs containing different rare earth metals and nearby elements (groups 2–4) were synthesized macroscopically using the most effective arc discharge method. However, many metal elements do not form EMFs in reasonable yield, but the reasons are still under investigation. During the past twenty years, EMFs have attracted great attention from chemists, physicists, materials scientists and even biologists for their unique structures, novel properties and potential applications in many disciplines of sciences [11–13]. In a review paper published last year, we summarized the status and developments of EMFs, especially focusing on the EMFs that had received concrete crystallographic characterizations [14]. However, due to the space constraints, many important results related to the structures and properties of EMFs were not included. Accordingly, in the current review paper, we do not disucss the X-ray structures of EMFs but mainly focus on those research results omitted from the former reviews [14].

2. Classification

According to the different species encapsulated inside the fullerenes, EMFs can be classified into mono-EMFs, di-EMFs, and cluster-EMFs. Additionally, cluster-EMFs are classifiable into several sub-branches depending on the composition of the internal metal clusters. Hetero-EMFs are also formed when one carbon atom in fullerene framework is replaced by a heteroatom such as N or B.

2.1. Mono-EMFs

Mono-EMFs are such compounds with only one metal atom trapped inside the carbon cage. They are the earliest discovered and most rapidly developed EMFs [15–19]. All the metal elements listed in Table 1 can form mono-EMFs [20–29]. Other metals, especially those with outstanding catalytic properties, will hinder the formation of fullerene cages, and thus cannot be capsulated inside fullerenes. In 1985, Heath et al. observed the ion peak of La@C_{60} in a mass spectrum of carbon soot and thus discovered the first mono-EMF [9]. Then Y@C_{82} was synthesized and characterized. It was discovered that the yttrium atom in Y@C_{82} could be displaced from the center of the C_{82} cage [30,31]. By encapsulating the metal atom in mono-EMFs, some unstable fullerene cages can be stabilized significantly, such as Ca@C_n ($n = 72, 74, 82, 84$) [32,33]. A small quantity of Li@C_{60} was produced by an improved ion implantation method and the result proved that the off-center displacement of Li^+ inside the cage could induce a large hyperpolarisability to the whole molecule [34]. Additonally, much attention has been paid to the separation and purification of EMFs. For example, a macroscopic quantity of Gd@C_{82} was isolated using high-performance liquid chromatography (HPLC) [35]. The mono-EMFs of Eu@C_{74} [36]