



## Review

## Carbon atoms trapped in cages: Metal carbide clusterfullerenes

Peng Jin<sup>a,\*\*</sup>, Chengchun Tang<sup>a</sup>, Zhongfang Chen<sup>b,\*</sup><sup>a</sup> School of Material Science and Engineering, Hebei University of Technology, Tianjin 300130, PR China<sup>b</sup> Department of Chemistry, Institute for Functional Nanomaterials, University of Puerto Rico, San Juan, PR 00931, USA

## Contents

1. Introduction .....	90
2. Conventional or unconventional? ( $M_m@C_{2n+2}$ vs. $M_mC_2@C_{2n}$ ) .....	90
2.1. $Sc_2@C_{70}$ vs. $Sc_2C_2@C_{68}$ .....	91
2.2. $Sc_2@C_{74}$ vs. $Sc_2C_2@C_{72}$ .....	92
2.3. $Sc_2@C_{80}$ vs. $Sc_2C_2@C_{78}$ .....	92
2.4. $Ti_2@C_{80}$ vs. $Ti_2C_2@C_{78}$ .....	92
2.5. $Sc_2@C_{82}$ vs. $Sc_2C_2@C_{80}$ .....	94
2.6. $Sc_3@C_{82}$ vs. $Sc_3C_2@C_{80}$ .....	94
2.7. $Sc_4@C_{82}$ vs. $Sc_4C_2@C_{80}$ .....	95
2.8. $Sc_2@C_{84}$ vs. $Sc_2C_2@C_{82}$ .....	96
2.9. $Y_2@C_{84}$ vs. $Y_2C_2@C_{82}$ .....	96
2.10. Other clusterfullerenes containing two entrapped carbons .....	96
2.11. Other clusterfullerenes containing one entrapped carbon .....	99
3. Novel structures and cluster–cage interplay .....	100
3.1. Compressed metal carbide clusters .....	100
3.2. Expanded and distorted cages .....	100
3.3. Electronic structure .....	101
3.4. Cluster–cage interplay .....	101
3.5. Effect of acetylide ion encapsulation .....	102
3.5.1. Bonding nature of the acetylide ion .....	102
3.5.2. $C_2$ NMR chemical shift .....	102
3.5.3. Effect of additional $C_2$ : $M_m@C_{2n}$ vs. $M_mC_2@C_{2n}$ .....	102
3.6. Cluster motion .....	102
4. Exohedral reactivity .....	104
5. Properties and potential applications .....	106
5.1. Electrochemical properties .....	106
5.2. Magnetic properties .....	107
5.3. Electronic transport properties .....	107
5.4. Potential applications .....	108
6. Concluding remarks .....	108
Acknowledgments .....	109
References .....	109

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## ABSTRACT

Metal carbide clusterfullerenes (MCCFs), which trap two carbon atoms together with metal atom(s) inside the fullerene cage, are a novel branch of endohedral metallofullerenes (EMFs). This review presents an exhaustive survey of recent research progress in MCCFs. After a detailed enumeration of the structural establishments of representative MCCFs, their novel structures, intriguing cluster–cage interplays, fascinating properties, and potential applications are highlighted. Moreover, a variety of new MCCF members are suggested for future identification.

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\* Corresponding author. Tel.: +1 7875526811.

\*\* Corresponding author.

E-mail addresses: [china.peng.jin@gmail.com](mailto:china.peng.jin@gmail.com) (P. Jin), [zhongfangchen@gmail.com](mailto:zhongfangchen@gmail.com) (Z. Chen).

## 1. Introduction

Endohedral metallofullerenes (EMFs) are novel nanomaterials enclosing a variety of metal ions or metal-containing clusters in various fullerene cages [1–3]. In the past two decades, EMFs have attracted widespread attention due to their unique structures and properties that are remarkably different from their parent cages. A ubiquitous feature of EMFs is the existence of substantial charge transfer from the encased species to the outer carbon frameworks. The negatively charged cages exhibit stabilities that are entirely different from those of the neutral cages. Thus, the formation of EMFs has been employed to help stabilize and synthesize many otherwise labile fullerenes that violate the isolated pentagon rule (IPR) [4] or are of large size [5,6]. More significantly, the physical and chemical properties of EMFs can be tuned by changing the encapsulated species, which endows EMFs with many promising applications in photovoltaics, spintronics, biomedicines, and functional materials [1–3].

Since the first experimental detection of  $\text{LaC}_{60}$  in 1985 [7], EMFs have a history only a few days shorter than the celebrated  $\text{C}_{60}$  buckyball [8]. EMFs can be classified in terms of the encapsulated species. Two classical types, monometallofullerenes (mono-EMFs) and dimetallofullerenes (di-EMFs), can be distinguished according to the number of the encased metals. The first stable mono-EMF  $\text{La@C}_{82}$  [9] and di-EMF  $\text{La}_2\text{@C}_{80}$  [10] were both isolated in 1991. Because the formal charge transferred from each metal to the cage is 3  $e$ , their electronic configurations can be denoted as  $\text{La}^{3+}\text{@C}_{82}^{3-}$  and  $(\text{La}^{3+})_2\text{@C}_{80}^{6-}$ , respectively. Thereafter, numerous conventional endofullerenes composed of different metals and cage sizes were successfully synthesized, isolated, and characterized. The encaged metals originate from Groups I to IV on periodical table, with lanthanide being the most popular.

In 1999, the first trimetallic nitride template (TNT)  $\text{Sc}_3\text{N@C}_{80}$  was accidentally discovered (due to  $\text{N}_2$  leakage into the arc discharge chamber) by Stevenson et al. and announced the birth of a brand-new branch of EMFs: clusterfullerenes [11]. Its production yield is lower than  $\text{C}_{60}$  and  $\text{C}_{70}$  and retains the most abundant EMFs thus far. The successful synthesis of  $\text{Sc}_3\text{N@C}_{80}$  drove a new wave of clusterfullerene fever [12]. To date, in addition to the classical metal nitride clusters ( $\text{M}_3\text{N}$ , such as  $\text{Sc}_3\text{N}$ ,  $\text{Y}_3\text{N}$ ,  $\text{Er}_3\text{N}$ , and  $\text{Gd}_3\text{N}$ ), the inner compositions have expanded to metal carbides ( $\text{M}_{2,3,4}\text{C}_2$ , e.g.,  $\text{Sc}_2\text{C}_2\text{@C}_{84}$ ) [13], hydrogenated metal carbides ( $\text{Sc}_3\text{CH}$ , e.g.,  $\text{Sc}_3\text{CH@C}_{80}$ ) [14], metal nitrogen carbides ( $\text{Sc}_3\text{NC}$ , e.g.,  $\text{Sc}_3\text{NC@C}_{80}$ ) [15], metal oxides ( $\text{Sc}_{2,4}\text{O}_{1,2,3}$ , e.g.,  $\text{Sc}_4\text{O}_2\text{@C}_{80}$ ) [16], and metal sulfides ( $\text{Sc}_2\text{S}$ , e.g.,  $\text{Sc}_2\text{S@C}_{82}$ ) [17]. These achievements have greatly enriched the EMF family.

During this “new gold rush era”, however, many previously assumed classical EMF structures were seriously challenged. The crisis began in 2001 from the breakthrough reassignment of a  $\text{Sc}_2\text{C}_{86}$  isomer, the previously assumed di-EMF  $\text{Sc}_2\text{@C}_{86}$  (I), as the first metal carbide clusterfullerene (MCCF)  $\text{Sc}_2\text{C}_2\text{@C}_{84}$  [13]. In this unprecedented molecule, a  $\text{C}_2$  pair is “abandoned” by the  $\text{C}_{84}$  cage carbons from constituting an otherwise  $\text{C}_{86}$  skeleton and is unusually trapped together with the Sc atoms inside the hollow. Following this prototype, a variety of new members have joined the MCCF community through experimental findings and/or theoretical predictions, including  $\text{Sc}_2\text{C}_2\text{@C}_{68}$  [18],  $\text{Y}_2\text{C}_2\text{@C}_{68}$  [19],  $\text{La}_2\text{C}_2\text{@C}_{68}$  [19],  $\text{Sc}_2\text{C}_2\text{@C}_{72}$  [20],  $\text{Sc}_2\text{C}_2\text{@C}_{78}$  [21],  $\text{Ti}_2\text{C}_2\text{@C}_{78}$  [22–24],  $\text{Zr}_2\text{C}_2\text{@C}_{78}$ ,  $\text{Hf}_2\text{C}_2\text{@C}_{78}$  [25],  $\text{Sc}_2\text{C}_2\text{@C}_{80}$  [26],  $\text{Sc}_3\text{C}_2\text{@C}_{80}$  [27,28],  $\text{Sc}_4\text{C}_2\text{@C}_{80}$  [29],  $\text{Sc}_2\text{C}_2\text{@C}_{82}$  (I, II, III) [30–32],  $\text{Y}_2\text{C}_2\text{@C}_{82}$  (I, II, III) [33,34],  $\text{ErY}_2\text{C}_2\text{@C}_{82}$  [35],  $\text{Er}_2\text{C}_2\text{@C}_{82}$  (I, II, III) [36],  $\text{Y}_2\text{C}_2\text{@C}_{84}$  [37–39],  $\text{Gd}_2\text{C}_2\text{@C}_{84}$  [39],  $\text{Sc}_2\text{C}_2\text{@C}_{86}$  [40],  $\text{Lu}_3\text{C}_2\text{@C}_{88}$  [41],  $\text{Sc}_2\text{C}_2\text{@C}_{90}$  [40],  $\text{Y}_2\text{C}_2\text{@C}_{92}$  [37,42],  $\text{Gd}_2\text{C}_2\text{@C}_{92}$  [43,44], and  $\text{Y}_2\text{C}_2\text{@C}_{100}$  [37]. A number of these MCCFs have been definitively characterized using single-crystal X-ray crystallography (Table 1). Currently, the synthesis and characterization of new

**Table 1**

Complete list of all reported MCCFs.

MCCFs	Single-crystal structure available?
$\text{Sc}_2\text{C}_2\text{@C}_{68}$	No
$\text{Y}_2\text{C}_2\text{@C}_{68}$	No
$\text{La}_2\text{C}_2\text{@C}_{68}$	No
$\text{Sc}_2\text{C}_2\text{@C}_{72}$	Yes
$\text{Sc}_2\text{C}_2\text{@C}_{78}$	No
$\text{Ti}_2\text{C}_2\text{@C}_{78}$	No
$\text{Zr}_2\text{C}_2\text{@C}_{78}$	No
$\text{Hf}_2\text{C}_2\text{@C}_{78}$	No
$\text{Sc}_2\text{C}_2\text{@C}_{80}$	Yes
$\text{Sc}_3\text{C}_2\text{@C}_{80}$	Yes
$\text{Sc}_4\text{C}_2\text{@C}_{80}$	No
$\text{Sc}_2\text{C}_2\text{@C}_{82}$	Yes
$\text{Y}_2\text{C}_2\text{@C}_{82}$	No
$\text{ErY}_2\text{C}_2\text{@C}_{82}$	No
$\text{Er}_2\text{C}_2\text{@C}_{82}$	No
$\text{Sc}_2\text{C}_2\text{@C}_{84}$	Yes
$\text{Y}_2\text{C}_2\text{@C}_{84}$	No
$\text{Gd}_2\text{C}_2\text{@C}_{84}$	Yes
$\text{Sc}_2\text{C}_2\text{@C}_{86}$	No
$\text{Lu}_3\text{C}_2\text{@C}_{88}$	No
$\text{Sc}_2\text{C}_2\text{@C}_{90}$	No
$\text{Y}_2\text{C}_2\text{@C}_{92}$	No
$\text{Gd}_2\text{C}_2\text{@C}_{92}$	Yes
$\text{Y}_2\text{C}_2\text{@C}_{100}$	No

MCCFs has become a notably active research area in fullerene chemistry.

Recently, comprehensive reviews have been published regarding conventional EMFs and/or clusterfullerenes [3], and there is also a short account of MCCFs [45]. In contrast to these contributions, this review article specifically focuses on the current research progress of MCCFs from both experimental and theoretical aspects. Particularly highlighted are the novel structures and fascinating properties that differ from conventional mono-, di-, and TNT EMFs. The synthesis (DC-arc discharge of a metal source/graphite composite rod) and separation (multi-step high-performance liquid chromatography (HPLC)) methods for MCCFs are not given in detail because they are the same as for traditional EMFs. For the sake of completeness, other single carbon-trapping clusterfullerenes, such as  $\text{Sc}_3\text{CH@C}_{80}$  [14] and  $\text{Sc}_3\text{NC@C}_{80}$  [15], are also covered.

## 2. Conventional or unconventional? ( $\text{M}_m\text{@C}_{2n+2}$ vs. $\text{M}_m\text{C}_2\text{@C}_{2n}$ )

As mentioned above, the story of MCCFs began with the structure characterization of  $\text{Sc}_2\text{C}_{86}$ , which was first detected in a mass spectrum by Shinohara et al. in 1993 [46]. Two isomers were isolated and were believed to adopt a classical di-EMF  $\text{Sc}_2\text{@C}_{86}$  form in their subsequent spectroscopic experiments [47]. This assumption was soon overturned by the  $^{13}\text{C}$  NMR spectrum measurement by the same group [13]. For  $\text{Sc}_2\text{C}_{86}$  (I) in  $\text{CS}_2$  solution, 12 lines (10 distinct lines of nearly equal intensity, one line with half the intensity, and an additional line with 1/4 the intensity) were observed (Fig. 1a). None of the 19 IPR isomers of  $\text{C}_{86}$  [48], however, can exhibit this spectral feature. Therefore, an alternative  $\text{Sc}_2\text{C}_2\text{@C}_{84}$  formula with a novel  $\text{Sc}_2\text{C}_2$  metal carbide unit inside an IPR-satisfying  $D_{2d}(51591)\text{-C}_{84}$  cage [49] was conceived (Fig. 1b).  $D_{2d}(51591)\text{-C}_{84}$  is also one of the most abundant  $\text{C}_{84}$  fullerenes. The  $^{13}\text{C}$  NMR spectrum was thus rationalized: 11 of the 12 NMR signals ( $\delta = 129.55\text{--}148.27$  ppm) stemmed from the parent  $\text{C}_{84}$  cage, whereas the signal at  $\delta = 92$  ppm was attributed to the internal  $\text{Sc}_2\text{C}_2$  moiety (which is actually due to an impurity as identified in a more sophisticated NMR measurement [50] and a density functional theory (DFT) study [51]). This revolutionary

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