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Endohedral Clusterfullerenes: Future Perspectives

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Although most endohedral fullerenes continue to be scientific curiosities for the most part, several are finding unique and promising applications due to their interesting physical and chemical properties. Herein, some future research directions and applications are described and discussed for this field.

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Endohedral metallofullerenes (EMFs) are molecular species that consist of an encapsulated metallic moiety within a fullerene carbon cage. Since the first stable endohedral metallofullerene, $La@C_{82}$, was detected by Smalley et al. in 1985, mono-EMFs and di-EMFs have been extensively studied. After the serendipitous discovery of $Sc_3N@C_{80,}$ the third most abundant fullerene that can be prepared using the Krätschmer-Huffman method, the study of EMFs has gradually shifted to the field of clusterfullerenes. Clusterfullerenes have found use in a wide range of applications. Specifically, clusterfullerenes have excellent potential in next generation photovoltaic devices and in biomedical applications, both as diagnostic and therapeutic agents. The complementary and synergistic relationship between the encapsulated clusters and their cages are responsible for the remarkable chemical and physical properties that these molecules display.[1] In this brief article, we describe some of the most recent progress in understanding the impact of cluster/cage interactions in determining structure and reactivity. We emphasize how these recent findings have enhanced our fundamental understanding and speculate how they define new trajectories for the field.

Structural Adaptability of Internal Clusters

Unlike mono and di-EMFs, clusterfullerenes contain metal and non-metal atoms (N, C) bonded to form encapsulated clusters within the carbon cages. As may be expected, this results in different metal-cage interactions compared to those observed for mono or di-EMFs. One of the most interesting characteristics of clusterfullerenes is the structural flexibility exhibited by some of the clusters. Clusters of nitride clusterfullerenes display varying degrees of pyramidalization as a direct result of the size of the incorporated metal. For example, the M_3N ($M = Sc, Lu$) clusters in I_h-C_{80} cages are planar, whereas larger nitride clusters ($M = Y, Gd$) in I_h-C_{80} cages are pyramidal with the nitrogen atom out of the plane of the three metal ions.[2,3] For metal carbide endohedrals, cage size directly influences the configuration and shape of the carbide cluster shape. Early crystallographic results showed that the M_2C_2 cluster normally exhibits a butterfly shape structure.[4–8] However, recently isolated carbide cluster metallofullerenes (CCMFs) have shown structural changes for relatively large $M_2C_2@C_{2n}$ cages.[4,9–13] Dorn and coworkers predicted that linear M_2C_2 cluster structures should be observed for relatively large fullerene cages of at least 100 carbons.[14] Very recently, a series of crystallographic structures have confirmed the computational prediction that increasing the size of the fullerene cage while maintaining the same encapsulated carbide cluster results in its elongation and deviation from its regular butterfly shape, transforming it into a zigzag structure (See Figure 1). The Sc_2C_2 cluster exhibits a folded butterfly shape inside $Sc_2C_2@C_{3v}(8)$-C_{82}[15,16] and $Sc_2C_2@D_{2d}(23)$-C_{84},[9,16] but a twisted and elongated structure in $Sc_2C_2@C_{2v}(9)$-C_{86}[10] and $Sc_2C_2@C_s(\text{hept})$-C_{88}.[11] Recent theoretical results from Popov et al. proposed that the distorted linear structure of M_2C_2, relative to the common butterfly-like shape, can be attributed to the long metal-metal distance, which induces a "nanoscale stretching" effect on the cluster.[17] In the future, detailed consideration of carbon cage sizes, geometries and metal-metal distances will be important to predict carbide cluster configurations in metallofullerenes. Fully stretched M_2C_2-type clusters are anticipated as predicted by Dorn et al.[14]

Endohedral Clusters Can Drastically Affect/Control Exohedral Functionalization Regiochemistry

In addition to the unique structural characteristics of the internal clusters, recent work has also shown that exohedral chemical functionalization of clusterfullerenes is strongly controlled by the encapsulated moieties.[18,19] These findings have led to a more in-depth understanding of the regioselectivity of multiple additions to clusterfullerenes, and to predictable structures. While bis-additions to empty fullerene cages produce large numbers of isomers, bis-additions to clusterfullerenes result in very few isomeric products. Surprisingly, out of 91 statistically possible bis-pyrrolidine regioisomers, only three were isolated for $Sc_3N@C_{80}$ and two for $Lu_3N@C_{80}$[19] (See Figure 2). This clearly demonstrates the strong influence of the cluster on the exohedral reactivity. While tethered bis-additions work very effectively on empty fullerenes, they fail with clusterfullerenes, clearly indicating that cluster control dominates over tether control.[19] Both experimental and theoretical studies have uncovered the reactive selectivity associated with five-membered rings and the importance of aromaticity in the chemistry of clusterfullerenes.[20–22] Therefore, for future cluster endohedrals, isomeric control will likely be done by refined cluster selective directivity.

Potential Applications of Clusterfullerenes

Obviously, the above-mentioned discoveries have added new insights to our understanding of endohedral fullerene structure and reactivity. More importantly, such understanding is critical to their successful implementation and utilization in practical applications. As shown by recent reports, there are several potential applications for endohedrals. For example, some water-soluble derivatives of gadolinium-containing metallofullerenes have shown great promise in innovative medical positron emission tomography/magnetic resonance (PTE/MR) simultaneous imaging techniques.[23] In vivo tests

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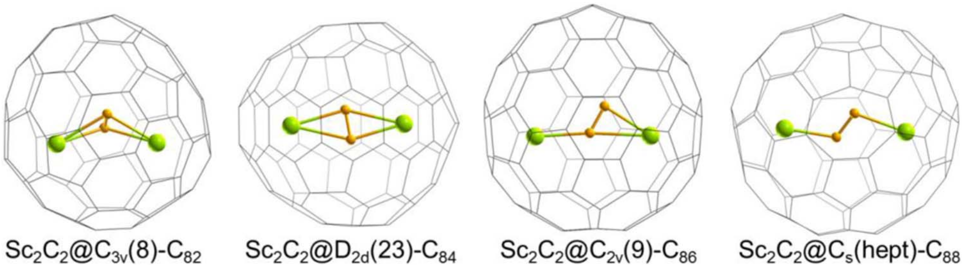

Figure 1. Crystallographic structures of Sc_2C_2-type endohedrals showing the tendency of the Sc_2C_2 carbide cluster to stretch from a butterfly shape to an elongated zig-zag structure.

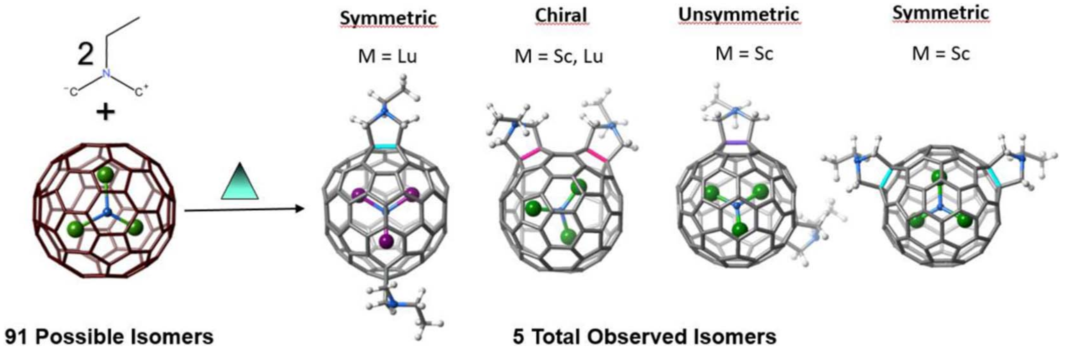

Figure 2. The 5 of 91 possible isomers produced by bis functionalization of M_3N@I_h-C_{80} with pyrrolidine.

of a Gd_3N@C_{80} derivative confirmed its effectiveness in providing contrast for tumor imaging.[24] Similar metallofullerenes, once chemically optimized, will likely serve as low-toxicity, highly specific medical imaging agents.

Organic photovoltaic (OPV) devices have incorporated fullerenes as efficient electron acceptors and conductors for many years with promising results.[25] Although many OPV devices with fullerenes as electron acceptors have been reported, only one example using a cluster containing endohedral has appeared.[26] Bis-functionalized fullerenes have also found use in OPV devices, however, regiomeric adduct control is a key factor in their effectiveness, thus developing methods for regiomeric control is very important. We foresee that by utilizing new knowledge of regioslectivity and cage/cluster interactions, functionalized endohedral fullerenes will lead to higher efficiencies in high performance OPV devices in the near future, including perovskite hybrid cells.

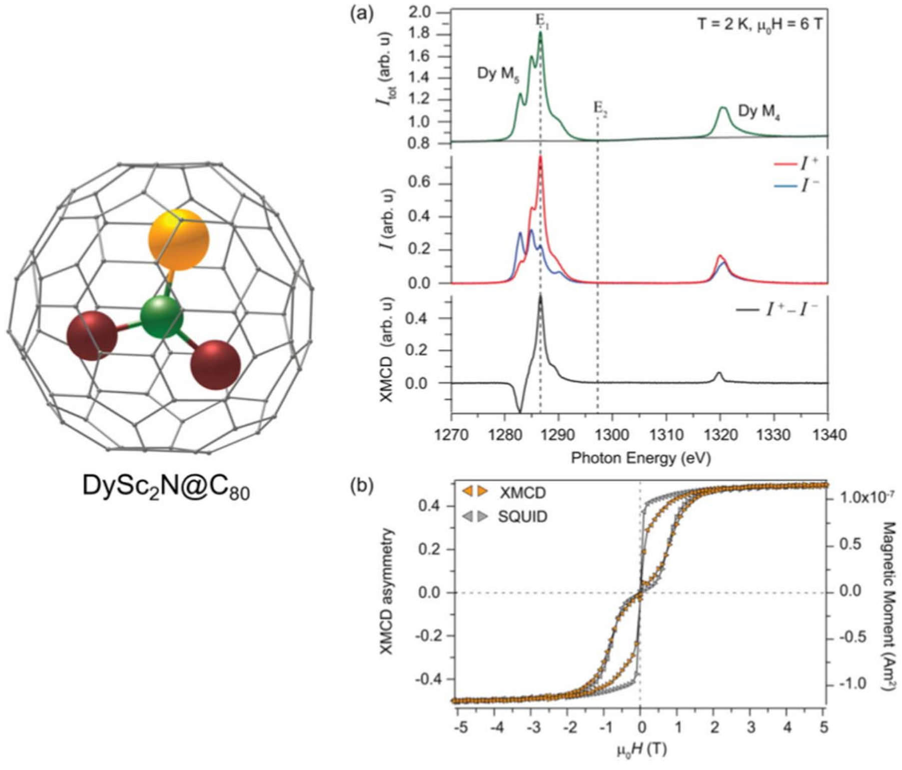

Figure 3. Left: chemical structure of $DySc_2N$@C_{80} (green, N; purple, Sc; orange, Dy). The C_{80} cage is shown as a wire frame. Right: (a) Top: Sum of X-ray absorption spectra of both X-ray helicities, I_{tot}, recorded at the Dy $M_{4,5}$-edge at 6 T. Middle: Polarization-dependent X-ray absorption spectra after subtraction of the background, I^+ (red) and I^- (blue). Bottom: XMCD spectrum, $I^+ - I^-$. (b) Magnetization curves recorded by XMCD and SQUID magnetometry at 2 K. (Reproduced with permission from Ref. 23.)

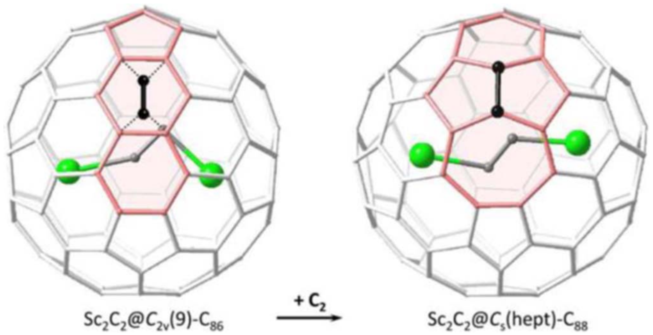

Figure 4. Structural relationship between $Sc_2C_2@C_{2v}(9)$-C_{86} and $Sc_2C_2@C_s$(hept)-C_{88} by a C_2 insertion. The motif that is involved in the transformation is highlighted in pink. The inserted C_2 unit is highlighted in black. (Reproduced with permission from Ref. 7).

Very recently, owing to their relatively long magnetic relaxation times (See Figure 3), the mixed-metal nitride clusterfullerenes $Dy_xSc_{3\text{-}x}N@C_{80}$ (x = 1–3) have received attention in the field of single-molecule magnets (SMM).[27–29] These compounds might find use in novel SMM based memory devices. Popov and co-workers found that a new type of μ_3-C mixed-metal carbide clusterfullerene, $Dy_2TiC@I_h$-$C_{80,}$ also exhibits SMM behavior.[30–32] However, the SMM properties of $Dy_2TiC_2@I_h$-C_{80} are less functional due to the presence of the second carbon atom in the central unit. In this regard, it is also anticipated that new carbide clusterfullerenes with $M_2C@C_{2n}$ compositions with unusual properties will be discovered in the near future.

Understanding Endohedral Fullerene Formation Mechanisms

Although endohedral metallofullerenes are of high interest due to their unique properties that offer promise in a variety of applications, industrial focus so far has been centered on the use of carbon nanotubes and graphene because of their relatively high production yields. To some extent, a lack of mechanistic understanding has hindered the development of metallofullerenes for industrial applications. Though still preliminary, recent ideas based on new discoveries could lead to improved synthetic processes and higher yields.

One mechanistic proposal postulates that high-symmetry fullerene cages can be formed via a cascade of C_2 extrusions from a non-classical fullerene cage in a top-down formation sequence.[33] The carbide cluster endohedral $Gd_2C_2@C_1(51383)$-C_{84} showed crystallographic propertied that support the top-down formation mechanism at the atomic level.[34] In contrast, Kroto and colleagues have proposed that metallofullerenes may form through an alternate, bottom-up formation mechanism. They showed that metallofullerenes can be formed via consecutive C_2 additions to small carbon nanoclusters and cages under a rich carbon vapor atmosphere.[35–37] However, there was no substantial physical evidence for the bottom-up growth model until the very recent work by Echegoyen, Poblet, Balch and colleagues which structurally characterized an endohedral carbide fullerene with a heptagon ring, $Sc_2C_2@C_s$(hept)-C_{88}, and proposed that it is a kinetically trapped intermediate in a bottom-up growth process from $Sc_2C_2@C_{2v}(9)$-C_{86}via a direct C_2 insertion (See Figure 4).[11] This is in perfect agreement with theoretical results which show that insertion of C_2 requires less energy than the corresponding Stone-Wales rearrangements.[38]

Since metallofullerene formation takes place in the gas phase at extremely high temperatures, further studies are required to establish more detailed mechanisms. Kroto predicted that C_2 loss events are also possible, for some cases, during a bottom-up reaction path.[36] Detailed mechanistic knowledge should prove useful to improve the production yields and thus overcome long-standing problems that hinder current and future applications of metallofullerenes.

Final Remarks

$Sc_3N@C_{80}$, discovered by Harry Dorn and co-workers in 1999, persists as the most abundant clusterfullerene known. It is perplexing that in the 17 years since its discovery, no other clusterfullerene has surpassed the synthetic yield of $Sc_3N@C_{80}$. Why is it that the first clusterfullerene discovered is also the most efficiently produced? Can a different clusterfullerene be designed which is higher yielding? What possible combination of parameters can be optimized to produce a more perfect complementary cluster/cage dynamic? Recent and future theoretical, structural and mechanistic advances in the field should lead to totally new compounds and to higher yielding ones. Given the complexity of the multiparametric space, including carbon cages of different sizes and shapes and the wide variety of different clusters, it seems statistically possible to prepare a multitude of novel compounds.

New synthetic discoveries, like those of the CCFMs, help us to establish a mechanistic understanding of how fullerenes may form. From results thus far, we see that not only can cluster composition direct cage chemistry, but that cage size and symmetry can also have a profound effect on the corresponding clusters. Such understanding is vital to our ability to rationally design fullerenes and endofullerenes to serve the next generation of material science developments. Endohedrals have already shown useful properties in the fields of organic photovoltaics and biomedical science. We look forward, and with great anticipation, to the next 17 years of clusterfullerene science and to the fundamental knowledge and practical applications that they will bring. The field is still in its early development stages.

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