



The Recent State of Endohedral Fullerene Research

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a Sc_2C_2 carbide cluster is included in a $\text{D}_{2d}\text{-C}_{84}$ cage (Fig. 2a). Meanwhile, dimetallofullerenes of scandium often reduce the larger cage size by forming a Sc_2C_2 cluster.⁶ As the existence of such a carbide cluster fullerene was also proved for a diyttrium structure with Y_2C_2 ,^{7,8} one asks whether only scandium and yttrium metals can form such carbides. Nevertheless the structures isolated so far show that metal carbide endohedral fullerenes represent a type of endohedral fullerenes with a cluster inside. Cages other than C_{82} demonstrably also encase the metal carbide inside.

Among the multimetallofullerenes, the $\text{Sc}_3\text{C}_2\text{C}_{82}$ structure was important as the three metal ions were shown by electron spin resonance (ESR) spectroscopy to be completely equivalent in the position and redox state of each of the scandium ions.⁹ Furthermore the position of the scandium ions inside the cage can be changed at lower temperatures as detected by ESR spectroscopy.¹⁰

As the equivalence of the three scandium ions inside the cage seemed to point to a balanced ordering of them, it was surprising that in a recent study a carbide endohedral fullerene was proposed by the group of Akasaka.¹¹ By NMR spectroscopy the authors have shown that a $\text{Sc}_3\text{C}_2\text{C}_{80}$ fullerene may exist with icosahedral cage symmetry (Fig. 2b). In this way the existence of a five atomic cluster in an endohedral fullerene has been proved. The question arises as to how large the cluster inside a fullerene cage can be. Is it a matter of size or a matter of chemical structure which determines the existence of a cluster inside the fullerene cage?

Extending the Cage Size

While it is expected that enlargement of the caged cluster could also stabilize larger cage sizes it was demonstrated in the frame of the synthesis of cluster fullerenes by Yang and Dunsch that instead, the di- and trimetallofullerenes (multimetallofullerenes) can result in the stabilization of a large series of higher fullerene cages. Thus they isolated for the first time the largest fullerene cage to date, a stable $\text{Dy}_2\text{C}_{100}$ dimetallofullerene at high yield as well as the largest trimetallofullerene ever isolated, Dy_3C_{98} .¹² Therefore, the extension of the sizes of both the conventional multimetallofullerenes and the encaged clusters opens new avenues in fullerene research. By extending the fullerene cage size with large structures of metals or clusters inside, another situation arises: the number of IPR-isomers is increasing (for C_{100} , there are 450 isomers) and the variety of structures

Since the last general reviews in the field of endohedral fullerenes by Shinohara in 2000¹ and by Akasaka and Nagase in 2002,² the variety of endohedral structures has been extended tremendously. With the turn of the millennium the world of endohedral fullerenes has changed in all respects. The research on the conventional endohedral fullerenes was predominately focused on structures with a single species such as metal ions encaged in the carbon cage like La@C_{82} . Such structures have been treated as a special type of a closed intercalation compound characterized by a doping process in which the electron transfer from the encaged metal ions to the carbon structure occurs. The charge separation in the form of $\text{La}^{3+}\text{C}_{82}^{3-}$ results in non-dissociating salts. The dissociation in this case was blocked for sterical reasons. Besides these monometallofullerenes which have been isolated as the first endohedral structures, noble gases from He to Kr and nonmetal atoms like N and P also have been incorporated. These structures form preferably C_{60} endohedrals, which are prepared under high pressure or by ion bombardment of the preformed fullerene cages. Unlike conventional metallofullerenes, all these endohedral fullerenes are uncharged.

How the charge at the fullerene cage can be changed by the incorporation of more than one metal ion as multicharged empty fullerenes exist in strong doping reactions, e.g., by potassium, was important to know. Thus many di- and trimetallofullerene

cages have been isolated. This group of multimetallofullerenes considerably extended the scope of the field by giving rise to completely new types of endohedral fullerenes.

The Non-IPR World

With the discovery of the dimetallofullerene, Sc_2C_{66} , it was shown for the first time by Shinohara's group that a dimetallo structure is sufficient to break the isolated pentagon rule (IPR), which is the stability rule for conventional fullerenes. As the C_{66} cage cannot form any IPR structure, there are fused pentagons in the non-IPR C_{66} (C_{2v}) cage (Fig. 1).³ Meanwhile, the same group showed that even fullerenes being able to form IPR cages are stabilized in a non-IPR form by a dimetallo structure: the endohedral La_2C_{72} fullerene.^{4a} The most recent non-IPR fullerene cage is based on a type of encaged species: the M_2C_2 cluster. (Sc_2C_2)@ C_{68} as reported by Wang *et al.*, for which a Sc_2C_2 carbide cluster is encaged in a non-IPR $\text{C}_{2v}\text{-C}_{68}$ cage.^{4b} Interestingly the isomeric structure of the non-IPR C_{68} cage proposed for (Sc_2C_2)@ C_{68} was different from that existing in the family of nitride cluster fullerenes and is discussed below in detail by Wang, *et al.*

The Carbide Structure

The story of stabilizing a C_2 moiety was first demonstrated for the dimetallofullerene, Sc_2C_{86} , which was $\text{Sc}_2\text{C}_2\text{C}_{84}$ as demonstrated by a nuclear magnetic resonance (NMR) study.⁵ The fullerene cage of (Sc_2C_2)@ C_{84} was first reported by Wang *et al.*, in which

of the metallofullerenes increases dramatically. Thus for $\text{Dy}_2\text{@C}_{100}$ at least six cage isomers must be taken into consideration (Fig. 3). While the variation of the number of cage isomers is not a preferable situation, the influence of cage size on physical properties and the behavior upon charging the fullerene is of high interest.

A New World of Cluster Fullerenes

A new world of cluster fullerenes was introduced by a synthesis which occurred by chance. While it was accepted in the fullerene community to avoid nitrogen as a cooling gas, the element was the key for a type of cluster fullerenes. Thus a class of endohedral fullerenes with a cluster inside was introduced as the trimetallic nitride endohedral fullerenes, with $\text{Sc}_3\text{N@C}_{80}$ being the first most abundant member. This structure was discovered in 1999 at a yield higher than all other endohedral fullerenes by introducing a small portion of nitrogen gas into the Krätschmer-Huffman generator during vaporization of graphite rods containing metal oxides.¹³ This method is called the trimetallic nitride template (TNT) process as proposed by the authors.¹³ In this nitride cluster fullerene as a type of endohedral fullerenes, the carbon cage adopts a caged trimetal nitride cluster structure which is not stable as a single molecule. The carbon cage of such an endohedral fullerene has an isomeric form which has not been isolated as an empty cage so far. The icosahedral C_{80} cage is stabilized by the electron transfer from the nitride cluster. Therefore, the trimetal nitride cluster structure and the icosahedral carbon cage appear to be stabilized by each other. The stabilizing effect of the nitride cluster is a further subject of detailed studies on the nitride cluster fullerenes to understand why such fullerenes are stabilized in these two ways.

Based on this method, several cluster fullerenes were produced like $\text{Er}_x\text{Sc}_{3-x}\text{N@C}_{80}$ ($x = 0-3$)^{13,14} and $\text{A}_x\text{Sc}_{3-x}\text{N@C}_{68}$ ($x = 0-2$; $\text{A} = \text{Tm}, \text{Er}, \text{Gd}, \text{Ho}, \text{La}$).¹⁵ In the latter case the trimetallic nitride is trapped in a non-IPR C_{68} cage.¹⁵ The $\text{Sc}_3\text{N@C}_{68}$ with the Sc_3N cluster encapsulated in a D_3 (isomer 6140) non-IPR C_{68} cage, as determined by X-ray crystallography and NMR spectroscopy (Fig. 4a),^{15,16} makes this fullerene particularly interesting. Besides the recent studies on theoretical calculations of the molecular structure of $\text{Sc}_3\text{N@C}_{68}$ on the basis of the ^{13}C NMR spectrum,¹⁷⁻¹⁹ a detailed study on its electronic and vibrational structures (Fig. 4b) with density functional theory (DFT) computations

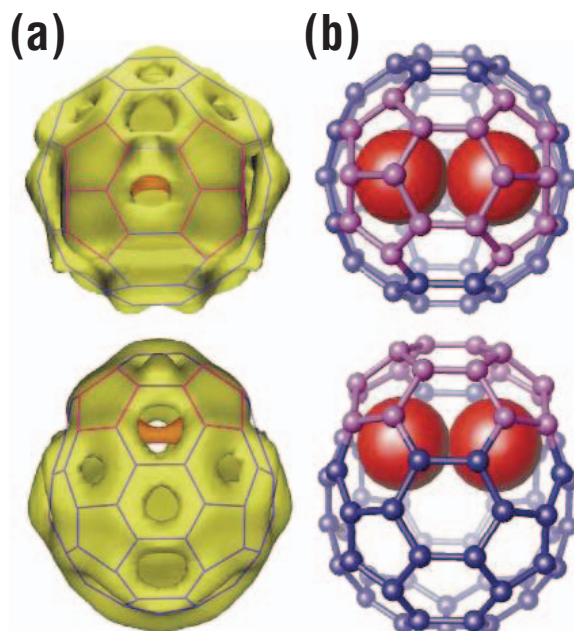


Fig. 1. (a) X-ray structure of the IPR-violating $\text{Sc}_2\text{@C}_{66}$ (C_{2v}) fullerene, showing a top view along the C_2 axis and a side view. (b) Calculated $\text{Sc}_2\text{@C}_{66}$ structures. (Adapted from Ref. 3.)

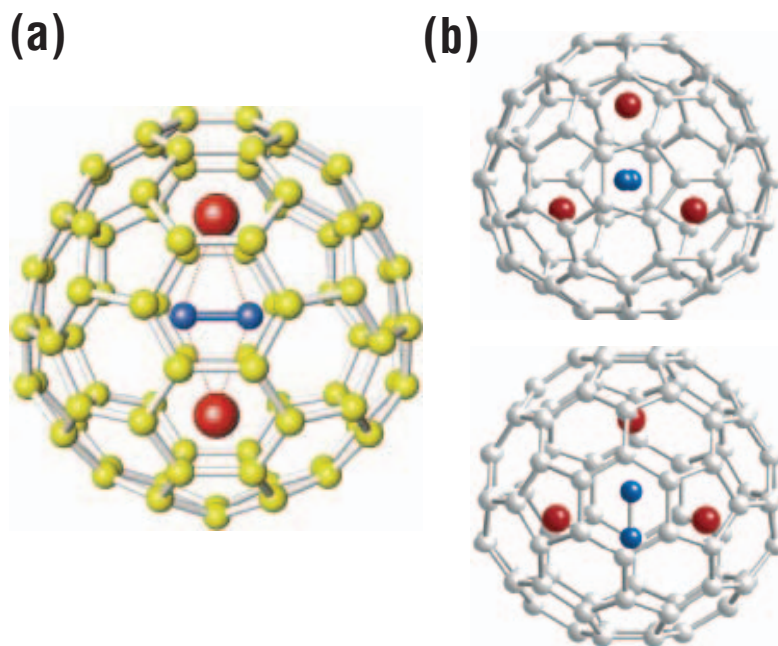


Fig. 2. (a) Schematic representation of the $(\text{Sc}_2\text{C}_2)\text{@C}_{84}$ (D_{2d}) molecule. (Adapted from Ref. 5.); (b) Structures calculated for $\text{Sc}_3\text{C}_2\text{@C}_{80}$ with two views. (Adapted from Ref. 11.)

was made by Yang *et al.* on the basis of high-yield synthesis by the reactive gas atmosphere procedure described below and a facile isolation.²⁰

Furthermore the following nitride cluster structures have been synthesized by the TNT method despite the relatively low yield of the nitride cluster fullerenes: $\text{Sc}_3\text{N@C}_{78}$,²¹ $\text{Lu}_3\text{N@C}_{80}$,^{22,23} $\text{Lu}_{3-x}\text{A}_x\text{N@C}_{80}$ ($x = 0-2$; $\text{A} = \text{Gd}, \text{Ho}$),²³ and $\text{Y}_3\text{N@C}_{80}$.²⁴

The standard arc discharge production of endohedral fullerene

structures described in the past resulted in very low yields. Generally, endohedral metallofullerenes yield 2% or less from the fullerene soot.^{1,2} The first description of the $\text{Sc}_3\text{N@C}_{80}$ fullerene formation by the TNT process claimed to secure a higher yield of the cluster fullerene in the soot extract ranging from 3 to 5%.¹³ While in the original work, air traces were used as a source of nitrogen, an improved route for nitride cluster fullerene must

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be searched based on other selective nitrogen sources.

The breakthrough was achieved by the development of the reactive gas atmosphere method in our group.²⁵⁻³¹ Here, by introducing NH_3 as the reactive gas, for the first time the nitride cluster fullerenes were produced as the dominant products in the soot, while the relative yield of the empty fullerene and conventional metallofullerenes was less than 5%.²⁵⁻³¹ In this way it has been demonstrated for the first time that the endohedral fullerene is the main product in the soot mixture, thus making the isolation of the endohedral fullerenes much more facile as only one separation step even by a simple chromatographic technique was needed. In applying this synthesis method the prerequisite for a successful application was fulfilled.

On the basis of the preferential production of the nitride cluster fullerenes, several large families of cluster fullerenes $\text{M}_3\text{N}@C_{2n}$ ($\text{M} = \text{Ho}, \text{Tb}, \text{Gd}, \text{Dy}, \text{Tm}$; $38 \leq n \leq 44$) specifically those cluster fullerenes with cages larger than C_{80} were isolated by our group.²⁶⁻³⁰

The Chemical Structure of Nitride Cluster Fullerenes

The isomeric structure of the first nitride cluster fullerene $\text{Sc}_3\text{N}@C_{80}$ (isomer I, I_h) was essentially determined by X-ray crystallography and ^{13}C NMR spectroscopic study.¹³ In particular, the Sc_3N cluster was demonstrated to have a planar structure.¹³ Likewise, the structure of the non-IPR cluster fullerene $\text{Sc}_3\text{N}@C_{68}$ and $\text{Sc}_3\text{N}@C_{78}$ was also well established.^{13,21} A recent study on $\text{Gd}_3\text{N}@C_{80}$ (isomer I, I_h) revealed that the Gd_3N was pyramidal despite the same symmetry of the C_{80} cage and $\text{Sc}_3\text{N}@C_{80}$ (isomer I, I_h).³² Although the isomeric structure of the cage has been well established,¹³⁻¹⁵ the structure and stability of the cluster and its charge transfer to the cage are rarely studied because such information would not be provided directly by X-ray crystallography and NMR spectroscopy. Recently, we demonstrated that vibrational spectroscopy is a powerful tool for the structural analysis of fullerenes not only due to its high structural sensitivity but also because of its higher temporal resolution compared to NMR spectroscopy.^{24-30,33,34} A series of nitride cluster fullerenes, $\text{M}_3\text{N}@C_{80}$ (I, II) ($\text{M} = \text{Sc}, \text{Gd}, \text{Dy}, \text{Tm}$), were studied systematically by vibrational spectroscopy and their isomeric structures were reasonably determined.^{24-27,29,33,34}

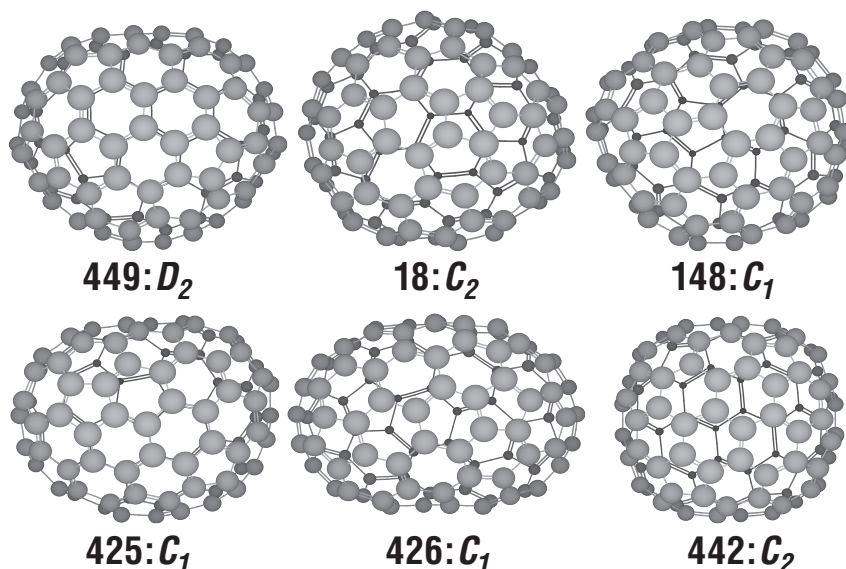


Fig. 3. Schematic structure models of the six probable cage isomers of $\text{Dy}_2@C_{100}$ (Dy atoms are omitted for simplification), which also represent the thermodynamically most stable IPR-isomers of the empty C_{100} fullerene. (Adapted from Ref. 12.)

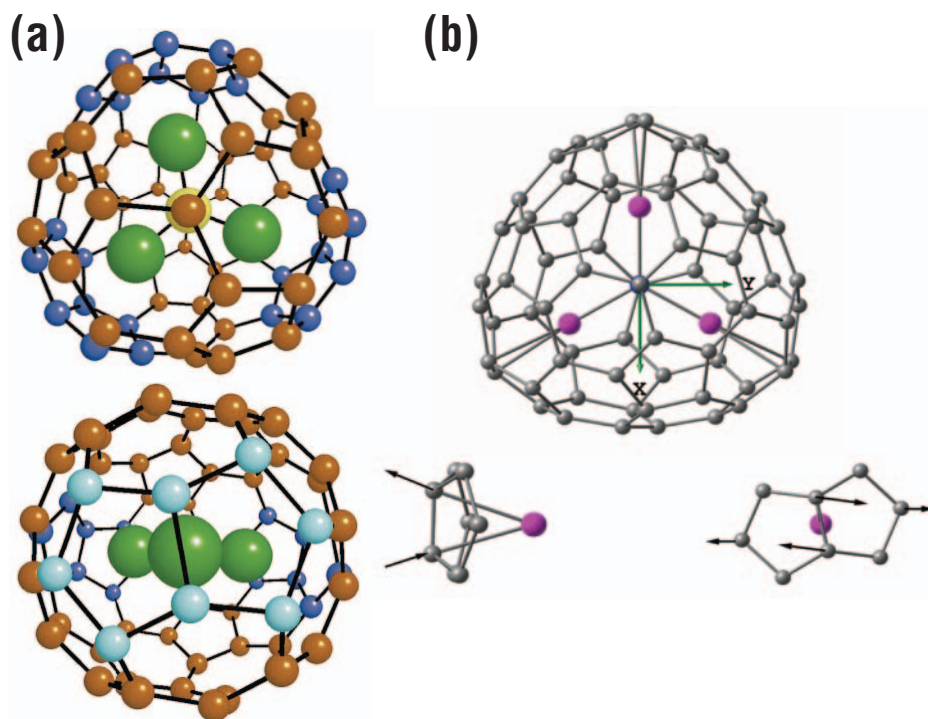


Fig. 4. (a) Two orthogonal views of $\text{Sc}_3\text{N}@C_{68}$ (D_3) structure generated from isomer 6,140 geometry (DFTB computation level) with encapsulation of the Sc_3N cluster. Views are shown from the C_3 axis (top) and the C_2 axis (bottom). (Adapted from Ref. 15.); (b) The proposed vibrational modes of the adjacent pentagons in $\text{Sc}_3\text{N}@C_{68}$ (D_3) (bottom). (Adapted from Ref. 20.)

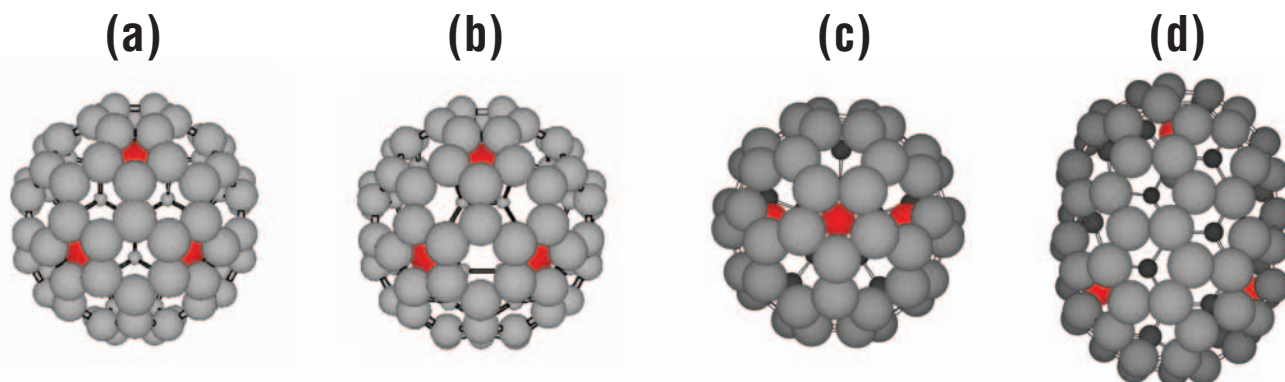


FIG. 5. Schematic structure model of three isomers of $\text{Dy}_3\text{N@C}_{80}$. (a) Isomer I (I_h); (b) Isomer II (D_{5h}). The most probable symmetry of the third isomer is proposed to be D_{5d} and shown in two views. (c) top view along the main C_5 axis assuming that one Dy atom locates on the C_5 axis; (d) front view. The Dy and C atoms are drawn in red and gray, respectively. The N atoms are hidden by the central C or Dy atoms. (Adapted from Ref. 29.)

On the basis of the reports on the coexistence of two isomers of $\text{M}_3\text{N@C}_{80}$ ($M = \text{Sc, Tm, Gd, Dy}$), which show different cage structures and electronic properties,^{24-27,33,34} and the theoretical prediction on the existence of 7 IPR-obeying isomers for C_{80} cage, we isolated successfully a third isomer of $\text{Dy}_3\text{N@C}_{80}$ with the most probable cage structure being $\text{C}_{80}:1$ (D_{5d}) (Fig. 5);²⁹ thus the stable isomeric structures of C_{80} cage were expanded.

The Properties of Nitride Cluster Fullerenes

The onset of visible/near-IR absorption of trimetal nitride C_{80} clusterfullerenes was studied to decide whether all nitride cluster fullerenes have any near-IR (NIR) absorptions and do behave like small bandgap materials as was claimed first for $\text{Sc}_3\text{N@C}_{80}$.¹³ No NIR absorption was observed, the onset of all the C_{80} nitride cluster fullerenes was similar, and the optical bandgaps were all higher than 1 eV. Therefore the nitride cluster fullerenes are stable compounds being nearly as stable as C_{60} .^{24,34}

The chemical reactivity of the nitride cluster fullerenes is similar to that of the conventional metallofullerenes. Thus the reaction of the C=C double bond can be used to derivatize the endohedral fullerene.² Besides, functionalized derivatives of $\text{M}_3\text{N@C}_{80}$ ($M = \text{Sc, Y, Gd}$) have also been reported.³⁵⁻³⁷

High-energy spectroscopy shows that $\text{Sc}_3\text{N@C}_{80}$ can be formally treated as a positively charged cluster inside a negatively charged icosahedral carbon

cage, i.e., $[\text{Sc}_3\text{N}]^{6+}@\text{C}_{80}^{6-}$.³⁸ Recent high-energy spectroscopic studies on a series of $\text{M}_3\text{N@C}_{80}$ (I) ($M = \text{Dy, Tm, Sc}$) revealed a significant discrepancy on the effective valence of the metal atom, i.e., 2.8, 2.9, and 2.4 for Dy, Tm, and Sc, respectively,³⁸⁻⁴¹ indicating their distinct difference on the charge transfer from the encaged cluster to the C_{80} cage. The electronic property and bandgap of nitride cluster fullerenes were comprehensively investigated by UV-vis-NIR spectroscopy and the strong influence of the cage isomeric structure and cage size on electronic structure of nitride cluster fullerenes has been elaborated.²⁷⁻³⁰

Generally, the vibrational structure is important for the characterization of the endohedral fullerenes because it is sensitively correlated to the isomeric structure of the cages. Moreover, the structure of the caged cluster could be probed by its vibrational pattern given by both infrared and Raman spectroscopy. Besides the study on the C_{80} -based nitride cluster fullerene $\text{M}_3\text{N@C}_{80}$ (I, II) ($M = \text{Sc, Gd, Dy, Tm}$),^{27,29,30,34,39} some nitride cluster fullerenes based on other cages such as $\text{M}_3\text{N@C}_{78}$ ($M = \text{Sc, Tm}$) were also investigated for detailed insights into their isomeric structures as well as their vibrational structures.^{30,34} A recent study on the electronic and vibrational structures of the non-IPR $\text{Sc}_3\text{N@C}_{68}$ was made by Yang *et al.*²⁰

The electrochemistry of a series of nitride clusterfullerene $\text{M}_3\text{N@C}_{80}$ (I) ($M = \text{Sc, Dy, Tm}$) was studied systematically to address the effect of the caged cluster on their

electrochemical behavior.^{33,34,39,42} Based on the comparison of the cyclic voltammograms of several tridysprosium $\text{Dy}_3\text{N@C}_{2n}$ ($2n = 78, 80$), i.e., $\text{Dy}_3\text{N@C}_{80}$ (I), $\text{Dy}_3\text{N@C}_{80}$ (II), and $\text{Dy}_3\text{N@C}_{78}$ (II), Yang *et al.* showed the effect of symmetry and size of the fullerene cage on the electrochemical behavior of $\text{Dy}_3\text{N@C}_{2n}$ ($2n = 78, 80$).⁴² The fascinating finding of this study is that the $\text{Dy}_3\text{N@C}_{80}$ (I) monoanion exhibits a charge-induced reversible rearrangement of the structure, which may result from the change of the Dy_3N cluster to a pyramidal form.⁴²

Outlook

Among the physical properties of endohedral fullerenes, the magnetic properties have not been largely explored despite their relevance to potential applications. The recent breakthrough on the high-yield production of nitride cluster fullerenes, however, has advanced this situation. The magnetic structure of $\text{M}_3\text{N@C}_{80}$ ($M = \text{Ho, Tb}$) has been investigated, in which the strong ligand fields within the M_3N cluster act on the ferromagnetically exchange-coupled moments of M. As a result of this combination of different types of interaction, the individual magnetic moments are not collinearly aligned but are parallel to the M-N bonds.^{43,44} A more recent study on the magnetic property of $\text{Dy}_3\text{N@C}_{80}$ (I) suggests strong Ising-like anisotropy due to crystal field and spin-orbit coupling.⁴⁵

The successful synthesis of peapods, i.e., nanotubes encapsulating fullerene

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molecules inside the core, has initiated a new branch of metallofullerene research. It is expected that the bandgap modulation in peapods generates conceptually new molecular devices, with different functionalities compared to empty single-walled nanotube (SWNT) electronic devices.⁴⁶⁻⁴⁸ Detailed information on such metallofullerene peapods as (EMF)_m@SWNTs (EMF = Gd@C₈₂, La₂@C₈₀, and Sc₂@C₈₄)

had been derived.⁴⁹⁻⁵¹ The change of conduction properties of SWNTs upon metallofullerene filling has been studied for (Dy@C₈₂)_m@SWNTs, showing the modulation of the electronic structure by the insertion of Dy@C₈₂ molecules and allowing the fabrication of novel transistors and rectifiers.^{52,53}

Projecting to the future of endohedral fullerenes research, this fast-growing field will undoubtedly reveal a large

variety of new chemical structures with exciting properties. Therefore breakthroughs in the application of endohedral fullerenes can be fully anticipated.

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