Since the experimental observation of the encapsulation of different species inside fullerene (endohedral fullerenes) cages, several research groups have focused on exploring the isolation of new compounds containing inert rare gas atoms and diatomic molecules. Advances in the entrapment of different species (such as inert rare gas atoms and diatomic molecules) inside fullerene cages have been accomplished since then.[2–7]

The discovery of a trimetallic nitride template endohedral metallofullerene (TNT EMF) by Stevenson et al. in 1999 revolutionized the field of endohedral fullerenes. More specifically, we discuss how the chemical and physical properties of these materials are affected as a function of the encapsulation of particular clusters, differences in fullerene size cages, and how exohedral functionalization changes their chemical and physical behavior.
Trimetallic nitride endohedral fullerenes

Since the discovery of the high-yielding TNT EMF, Sc₃N@C₈₀, many other endohedral families have been prepared over the past years. The incarceration of metallic nitride clusters inside carbon cages is performed by packing graphite-rods with metal oxides and arc-burning them under a nitrogen source gas (N₂ or NH₃) in a Krätschmer–Huffman arc reactor (Fig. 1).[8] The resulting carbon soot is extracted with suitable organic solvents (toluene, carbon disulfide, xylenes, etc.) to afford a mixture of empty cages and endohedral metallofullerenes. The latter are usually obtained as mixtures of M₃N@C₂ₙ (38 ≤ n ≤ 44) where the C₈₀ cage is the most abundant because of charge transfer stabilization between the metal cluster and the carbon cage.[56] An interesting observation is that empty Ih- and D₅h-C₈₀ cages have never been isolated, nor has Sc₃N outside the carbon cages. Out of the seven possible constitutional isomers for C₈₀ that obey the IPR rule, only the stable empty cages D₂ and D₅d have been isolated.[57,58] On the other hand, the two least stable empty isomers, Ih and D₅h, are the predominant ones when encapsulating the metallic clusters. Along with the isolation of the most abundant M₃N@C₈₀...
cage, higher fullerenes are also formed but at significantly lower yields, which have limited the study and characterization of these cages. Nevertheless, some higher metallic nitride fullerenes have been isolated and studied.[25,31,49,51,59-64] Higher metallic nitride endohedral fullerenes M3N@C2n, (M = La, Dy, Tm, Nd, Gd, Pr, Ce, Y; 40 \leq n \leq 55) have been studied extensively. Interestingly, their electrochemical behavior is different from those of the corresponding smaller cages. Our group reported the first electrochemical study of higher endohedral metallofullerenes and the first electrochemical studies for the gadolinium nitride endohedral fullerene family, Gd3N@C2n (n = 40, 42 and 44).[64] This family spans from small cages such as C78 to larger ones, such as C88. As shown in Fig. 2, isolated fractions 2, 4 and 7 were identified by Matrix Assisted Laser Desorption Ionization–Time of Flight Mass Spectrometer (MALDI–TOF MS) as Gd3N@C78 (n = 40, 42, 44), respectively.

The UV–vis of these three EMFs indicates that the band gap for Gd3N@C78 decreases as the cage size increases (Table 1). Interesting observations are derived from their redox potentials and their electrochemical band gaps. Figure 3 shows the cyclic voltammograms for Gd3N@C80, Gd3N@C84 and Gd3N@C88. Gd3N@C80 and Gd3N@C84 exhibit similar electrochemical behavior, but Gd3N@C88 exhibits two reversible reduction and two oxidation processes. The reduction potentials are similar to those of the smaller cages, but the first oxidation potential is shifted cathodically as the cage size increases (Table 1). The results of this study led to the conclusion that the reduction processes are mainly localized on the encapsulated metal cluster, whereas the oxidation process is mainly localized on the cage, which is different for every compound.[65]

In the TNT EMF families, the common preferential templating of the C80 cage can be explained by the widely accepted ionic model (see section on Theoretical Studies), which assumes a charge transfer from the metallic cluster to the fullerene cage resulting in mutual electronic stabilization. Our group reported the first preferential templating of a larger cage, C88, in the case of Nd3N@C2n (40 \leq n \leq 49).[63] The isolation of this new family of EMFs provided insight about how the encapsulated metal clusters affect the fullerene cage sizes. As the metal radius increases, the yield of the C80 cage decreases considerably while the formation of larger cages is enhanced. This was clearly observed for the larger family of Nd, Pr and Ce-based EMFs.[61] As shown in Fig. 4, the preferentially templated cage is C88, and as the metal size increases (from Nd to Pr to Ce), the abundance of higher endohedral fullerene cages gradually increases as well. This is very clear in the case of the Ce3N@C2n family, in which Ce3N@C88 is the second most abundant species within the family. Later on, we found that in the case of the La3N@C2n family, the C96 cage predominates, and C88 is the second most abundant.[66] No C80

![Figure 3. Cyclic voltammograms of Gd3N@C2n (n = 40, 42, 44) in 0.05 M of TBNPF6/DCB at 100 mV/s scan rate. “Reprinted with permission from Chaur et al., Journal of the American Chemical Society, 2007, 129, 47, 14826. Copyright 2007 American Chemical Society”](image)

![Figure 4. High-performance liquid chromatography chromatograms of the Nd3N@C2n (top), Pr3N@C2n (middle) and Ce3N@C2n (bottom) Endohedral metallofullerene families. y*: Pr@C84, y*: Ce@C84. Conditions: eluent = toluene, flow rate = 4.0 ml min⁻¹; Buckyprep-M column; detection wavelength = 372 nm. “Reprinted (adapted) with permission from Chaur et al., Chemistry – A European Journal, 2008, 14, 459”](image)

<table>
<thead>
<tr>
<th>TNT EMF</th>
<th>UV–vis onset (nm)</th>
<th>Band gap (eV)</th>
<th>Redox potentials (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd3N@C80</td>
<td>780</td>
<td>1.60</td>
<td>+0.58&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Gd3N@C84</td>
<td>1375</td>
<td>0.90</td>
<td>+0.32&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Gd3N@C88</td>
<td>1495</td>
<td>0.83</td>
<td>+0.06&lt;sup&gt;b&lt;/sup&gt; +0.49&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Nd3N@C88</td>
<td>1420</td>
<td>0.87</td>
<td>+0.07&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Pr3N@C88</td>
<td>1445</td>
<td>0.86</td>
<td>+0.09&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ce3N@C88</td>
<td>1442</td>
<td>0.86</td>
<td>+0.08&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Table 1. UV–vis onset, band gaps and redox potentials for M3N@C2n (M = Gd, Nd, Pr, Ce; n = 40, 42, 44) endohedral families

<sup>a</sup>Band gap calculated from the spectral onset; band gap (eV) \approx 1240/onset (nm).

<sup>b</sup>Denotes half-wave potentials.
cage is large EMFs families resulted in the observation of reversible reduction processes for the C88 cage but irreversible reduction processes for the smaller cage, and the oxidation potentials were lower for the larger cages (Fig. 5). These results are in agreement with the Gd3N@C88 electrochemical behavior (Table 1), proving that the reduction processes are based on the metal cluster and the oxidation processes are based on the carbon cage.

The question of whether higher metallic clusters can template higher fullerene cages, C2n (n > 49), was resolved by our group with the case of La3N@C2n (43 ≤ n ≤ 55) family, which is the first report of the La3N cluster encapsulated inside fullerene cages. The C96 cage predominates for the La3N cluster. The La3N@C2n family is composed of fullerene cages as low as C88 and as high as C104 from which only three fractions were isolated and purified, and identified by MALDI-TOF MS as La3N@C88, La3N@C92 and La3N@C96. The observed trend leads to the prediction that the next preferentially templated cages, if larger metals are used, would be the C104 cage. Interestingly, as the metal size increases, preferential templating goes from the C80 cage to C88, the C96 and apparently C104 would be the next one. This increase in size by eight carbons when the metallic cluster is increased seems to be a trend that remains unexplained. As discussed before, the electrochemical behavior of M3N@C88 is reversible in both reductive and oxidative processes for the smaller cage, and the oxidation potentials were higher fullerene cages, C2n (n > 49), La3N@C88 exhibits irreversible oxidation and reduction steps unlike the other M3N@C88 (Fig. 6 and Table 1). On the other hand, La3N@C92 and La3N@C96 exhibit similar electrochemistry and HOMO–LUMO gaps.

**Metallic sulfide endohedral fullerenes**

Endohedral metallofullerene syntheses have gone beyond the nitride families; metallic oxides, metallic carbides and recently metallic sulfides have also been synthesized and characterized. Dunsch et al. reported the first metallic sulfide cluster fullerene M2S@C82 (M = Sc, Y, Dy and Lu) using CH3N3 as a solid sulfur source. The only M2S@C82 cage isomer observed was determined to be the IPR (C3v:8).

Recently, our group reported the synthesis of the extended endohedral fullerene family, Sc2S@C2n (n = 40–50) in macroscopic quantities by the introduction of SO2 instead of a solid compound as the sulfur source. Two different high-performance liquid chromatography (HPLC) fractions contain Sc2S@C82 as the major component, but their large difference in HPLC retention times is indicative of two completely different isomers. The isolation of two isomers, the reported Sc2S@C82 (C3v:8) and a new isomer Sc2S@C82, were identified as the most abundant species within the family. It is known that electronic absorption of metallofullerenes is due to π–π* transitions of the fullerene cage; thus, correlations between the cage symmetry and the UV–vis absorptions are easily established. The UV–Vis–NIR spectra of both isomers showed that one of them was the reported C3v:8, whereas the other was assigned as the C2v:6 cage based on spectroscopic similarities with those of the previously reported Y2C2@C82. Density functional theory (DFT) calculations have shown that a formal charge transfer of 4 electrons from the metal cluster to the carbon cage occurs for metallic sulfide endohedral fullerenes. Prior studies with empty IPR C82 and C2v:6 fullerenes have shown that isomer 8 with C3v symmetry is the lowest energy species when the fullerene has a 4- charge electron. On the other hand, isomers C2v:9 and C2v:6 are the second and third lowest energy species. After encapsulation of the Sc2S moiety, the experimentally observed C3v:8 and C2v:6 isomers have similar stabilities, in agreement with the isolation of the two isomers. The two Sc2S@C82 isomeric cages were confirmed by X-ray crystallography by Mercado et al., and electrochemical and computational studies were reported. The crystallographic
studies revealed that both isomers contain fully ordered carbon cages. Additionally, $\text{Sc}_2(\mu_2-S)@C_{6v}(8)-C_{82}$ revealed two slightly different cage sites and a fully ordered $\text{Sc}_2S$ moiety in one of these sites, which is the first example in the endohedral fullerene families where both the carbon cage and the internal cluster moiety are fully ordered (Fig. 7). The $\text{Sc}_2S$-$\text{Sc}$ angles in $\text{Sc}_2(\mu_2-S)@C_{6v}(6)-C_{82}$ and $\text{Sc}_2(\mu_2-S)@C_{3v}(8)-C_{82}$ are 113.84(3)$^\circ$ and 97.34(13)$^\circ$, respectively. The remarkable differences were also predicted by computational studies, and this is the first case where the structure of a fullerene cage isomer is observed to exert an evident effect on the geometry of the encapsulated cluster. The electrochemical behavior of both isomers ($C_{3v}(8)$ and $C_{6v}(6)$) is significantly different. $\text{Sc}_2(\mu_2-S)@C_{6v}(6)-C_{82}$ exhibits an almost reversible first reduction potential, whereas the one for $\text{Sc}_2(\mu_2-S)@C_{3v}(8)-C_{82}$ is completely irreversible, but a well-defined fourth reduction peak not observed for the $\text{Sc}_2(\mu_2-S)@C_{6v}(6)-C_{82}$ is observed for the $\text{Sc}_2(\mu_2-S)@C_{3v}(8)-C_{82}$ isomer (Fig. 8). The differences in the electrochemical behavior are more pronounced for the oxidation processes. The oxidation peaks for the $\text{Sc}_2(\mu_2-S)@C_{3v}(8)-C_{82}$ are dramatically shifted anodically with respect to those for the $\text{Sc}_2(\mu_2-S)@C_{6v}(6)-C_{82}$ isomer. This shows a remarkable difference in their HOMO orbital energies that can be related to the different electronic structures. A comparative study was carried out between $\text{Sc}_2(\mu_2-S)@C_{6v}(6)-C_{82}$ and $\text{Sc}_2(\mu_2-O)@C_{6v}(6)-C_{82}$, where the influence of the nonmetal atom (O vs S) in the cluster on the electrochemical behavior was observed. This study revealed that compounds have similar HOMO and LUMO energies, not surprising because both compounds have the same cage symmetry and the endohedral clusters are isoelectronic.

Very recently, our group reported the first example of a non-IPR metallic sulfide endohedral fullerene (see section on Non-IPR endohedral metallofullerenes). This dimetallic sulfide cluster in a $C_{72}$ cage, $\text{Sc}_2S@C_{72}$, was assigned to the $C_{1}$ symmetry on the basis of crystallographic analysis. Computational studies confirmed that a formal charge transfer of four electrons from the encapsulated moiety, $\text{Sc}_2S$, to the fullerene cage occurs in $[\text{Sc}_2S]^{+4}@[C_{72}]^{-4}$. $^{37,68}$ $^{45}\text{Sc}$ NMR reveals a single signal, which suggests that both scandium atoms are either statically equivalent or that fast rotation of the cluster averages the signals in the NMR time scale. Computational studies agree with the crystallographic results, which show the two scandium atoms pointing to vicinal pentalene units. The electrochemical behavior is very different from those of the metallic sulfide endohedral fullerenes studied before. $\text{Sc}_2(\mu_2-S)@C_{6v}(6)-C_{82}$ and $\text{Sc}_2(\mu_2-S)@C_{3v}(8)-C_{82}$, The reductive scan for $\text{Sc}_2(\mu_2-S)@C_{6v}(6)-C_{82}$ is irreversible, which is not common for metallic endohedral fullerenes (Fig. 7). Additionally, the oxidative scan shows one reversible oxidation followed by a
second irreversible oxidation step. An interesting observation is that the presence of a second re-reduction step is observed if the oxidation scan is taken to the second oxidation step.

**Metallic oxide endohedral fullerenes**

The first metallic oxide endohedral fullerene was reported by Stevenson et al., and X-ray crystallography determined the structure as $\text{Sc}_4(\mu_3-O)_2@h-C_{80}$. There is only one example of an electrochemical study of a metallic oxide endohedral fullerene, that is the case of $\text{Sc}_4(\mu_3-O)_2@C_{60}$. We recently recorded the electrochemical behavior of $\text{Sc}_2\text{O}_2@h-C_{80}$ which is reported here for the first time, and found an interesting and rather unexpected behavior. The reductive scan shows two reversible reduction steps, which is uncommon for $h-C_{80}$ based compounds (Fig. 9). The OSWV experiment shows three reductions with a separation of approximately 0.63 V. This is also different from C80 TNT EMFs where the gap between the first and second reduction processes is smaller than the gap between the second and third reduction processes. The oxidation scan shows two reversible oxidation steps, and the first one overlaps with that for the commonly used internal reference, the redox couple for ferrocene, $\text{Fc/Fc}^+\text{,}$ so they have the same oxidation potential. The electrochemically determined HOMO – LUMO gap of 1.10 V is one of the lowest observed for an endohedral cluster fullerene.

**Non-IPR endohedral metallofullerenes**

Out of thousands of possible non-IPR isomers that can exist for a particular number of carbons in a fullerene, usually one isomer is overwhelmingly preferred for a particular cluster. Our group has reported non-IPR cages for metallic nitrile and metallic sulfide endohedral fullerenes. The egg-shaped endohedral fullerene $\text{Gd}_3\text{N}@C_{39}(39663)-C_{82}$ is one of the two isomers previously predicted by computational studies to be stable for a C82 cage with a 6- charge electron. X-ray crystallography showed a planar $\text{Gd}_4\text{N}$ cluster unit, where one of the gadolinium ions is pointing directly to the vicinal pentagene unit. The latter observation is a common feature for endohedral fullerenes with non-IPR cages; the metals are found to be pointing to the pentagon–pentagon junctions in all cases.

Other egg-shaped fullerenes were reported by our group, the case of $\text{Tm}_3\text{N}@C_{51}(31365)-C_{84}$ and $\text{Gd}_3\text{N}@C_{51}(31365)-C_{84}$. These endohedral fullerenes utilize the same cage symmetry (C3v) of the previously reported $\text{TB}_3\text{N}@C_{51}(31365)-C_{84}$, suggesting that it is the electron transfer from the cluster to the cage, rather than the nature of the encapsulated metallic nitrile cluster that dictates the preferential templating of a particular cage, as noted from computational studies. As in the case of $\text{Gd}_3\text{N}@C_{39}(39663)-C_{82}$, the internal cluster adopts a planar geometry, where one thulium atom in $\text{Tm}_3\text{N}@C_{51}(31365)-C_{84}$ and one gadolinium atom in $\text{Gd}_3\text{N}@C_{51}(31365)-C_{84}$ is pointing directly to the pentagon–pentagon fusion.

The first structural study of the non-IPR $\text{Gd}_3\text{N}@C_{22}(22010)-C_{78}$ isomer by X-ray crystallography was also reported by our group. Several endohedral fullerenes with a C78 cage had been structurally studied, but the majority possess a $D_{5h}(5)-C_{78}$ cage symmetry. Unexpectedly, two violations to the IPR were observed. The presence of two violations to the IPR and the ability of the cage to accommodate a planar $\text{Gd}_4\text{N}$ in such a small cage is an interesting feature of this metallic nitrile endohedral compound. As for the previously discussed non-IPR endohedral fullerenes, two gadolinium atoms point each to the two pentagon–pentagon junctions, and the third one points exactly to the middle of a hexagon ring (Fig. 10).

As previously discussed, our group reported the first non-IPR dimetallic sulfide cluster endohedral fullerene, $\text{Sc}_2\text{S}@C_{10}(10528)-C_{22}$. As for all non-IPR endohedral fullerene cages, the scandium ions were found to point to the vicinal pentagene units, which is a permanent characteristic of non-IPR endohedral fullerenes.

**CHEMICAL FUNCTIONALIZATION OF ENDOHEDRAL METALLOFULLERENES**

Many research groups have studied functionalization of endohedral fullerenes extensively. The study of how the chemical and physical properties of endohedral fullerenes change due to exohedral derivatization is important for potential applications of these compounds. Additionally, exohedral functionalization has helped in the characterization of new endohedral fullerene cages that could not be isolated and characterized in their unfunctionalized form. Functionalization also improves the solubility of endohedral fullerenes, which expands the range of possible potential applications as well.

The exohedral derivatization of endohedral fullerenes includes the use of Diels–Alder reactions, 1,3-dipolar cycloadditions, Bingel–Hirsch reactions, photochemical reactions, free-radical reactions...
and electrochemical reactions, among others. Herein, we focus on the exohedral functionalizations performed in our research group.

Cycloaddition reactions

$[3 + 2]$, 1,3-dipolar cycloadditions

In 2005, our research group reported the first pyrrolidine mono-adduct of $\text{Sc}_3\text{N@}_{h}\text{-C}_{80}$ and $\text{Y}_3\text{N@}_{h}\text{-C}_{80}$.\cite{77,78} The pyrrolidine adduct of $\text{Sc}_3\text{N@}_{h}\text{-C}_{80}$ was synthesized by means of the addition of an excess of N-ethylglycine and enriched $^{13}\text{C}$-paraformaldehyde in refluxing o-DCB. The corresponding fulleropyrrolidine mono-adduct was purified by column chromatography and characterized by different NMR techniques, such as, $^1\text{H}$, $^{13}\text{C}$ and heteronuclear multiple quantum coherence. NMR studies revealed that the addition of the addend occurred at a [5,6] double bond on the basis of the symmetry observed in the NMR spectrum. These results agree with the previously reported Diels–Alder adduct of an $h\text{-C}_{80}$ cage reported by Dorn and co-workers.\cite{79,80}

Later in 2005, our research group reported the first pyrrolidine derivative of $\text{Y}_3\text{N@}_{h}\text{-C}_{80}$.\cite{78} In this case, the addition of the pyrrolidine adduct under identical conditions as those reported for the $\text{Sc}_3\text{N@}_{h}\text{-C}_{80}$ case occurred at a [6,6] bond exclusively as determined by NMR studies, which revealed unsymmetrical pyrrolidine carbons and symmetrical geminal protons. These results indicate that the reaction of endohedral fullerenes is exquisitely controlled by the nature of the encapsulated cluster. The quantitative thermal isomerization of the [6,6] to the [5,6] adduct of $N$-ethylpyrrolidino-$M_3\text{N@}_{h}\text{-C}_{80}$ ($M = \text{Y, Er}$) was reported by our group as well.\cite{81} Thus, the [6,6] isomer is the kinetic product in the case of $\text{Y}_3\text{N@}_{h}\text{-C}_{80}$ whereas the [5,6] isomer is the thermodynamic product for both $\text{Y}_3\text{N@}_{h}\text{-C}_{80}$ and $\text{Sc}_3\text{N@}_{h}\text{-C}_{80}$. Both isomers were studied by NMR and electrochemical techniques.

$[2 + 1]$, cyclopropanation reactions

Cyclopropanation reactions, also known as Bingel–Hirsch reactions, on fullerenes are one of the most used strategies for the functionalization of endohedral fullerenes.\cite{82–84} The access to different malonic acid derivatives makes this approach a simple method for preparing different adducts. Attempts to perform this reaction on $M_3\text{N@}_{h}\text{-C}_{80}$ ($M = \text{Y, Er}$) succeeded in our group and afforded the first mono-methanofullerene derivatives.\cite{77,81} Electrochemical studies concluded that the addition had occurred on a [6,6] bond. This addition regiochemistry was confirmed by X-ray diffraction, which additionally showed a broken bond where the addition took place in the $\text{Y}_3\text{N@}_{h}\text{-C}_{80}$ derivative (Scheme 1). One of the metal ions in the cluster points directly to the open bond, which can partially explain the stability of the [6,6] open adduct.\cite{85} Attempts to perform this reaction under the same conditions with $\text{Sc}_3$.

Figure 10. (Top) Two orthogonal views of $\text{Gd}_3\text{N@}_{C_{2}}(22010)-\text{C}_{78}$ with abutting pentagons highlighted in turquoise, the nitrogen atom in blue and the gadolinium atoms in green. (A) View down the noncrystallographic twofold axis of the carbon cage. (B) Side view with the twofold axis in the vertical direction. Only the major gadolinium sites and the major cage orientation are shown. (Bottom) Drawing showing the position of the major $\text{Gd}_3\text{N}$ unit relative to the nearest carbon atoms of the fullerene cage in $\text{Gd}_3\text{N@}_{C_{2}}(22010)-\text{C}_{78}$. Distances are given in Å. *Reprinted with permission from Chaur et al., Journal of the American Chemical Society, 2009, 131, 11519. Copyright 2009 American Chemical Society*
N@h-C80 failed. The latter was attributed to the nature of the incarcerated cluster, which can exert an effect on the reactivity of the endohedral fullerenes towards exohedral functionalization.

Recently, our group succeeded in performing the Bingel-Hirsch functionalization of Sc3N@h-C80 and Lu3N@h-C80 in high yields using relatively typical conditions. The key ingredient of the modified approach, which we call the Pinzón-Bingel-Hirsch reaction, consists in adding dimethyl formamide as part of the solvent mixture, which leads to the preparation of the desired reaction, consists in adding dimethyl formamide as part of the solvent mixture, which leads to the preparation of the desired product. This result was attributed to the possibility of the presence of a carbene intermediate when 2,2-dibromo malonate was used. This result was attributed to the possibility of the presence of a carbene intermediate when 2,2-dibromo malonate was used.

In 2008, our group explored the reactivity of larger endohedral fullerenes of the Gd3N@h-C80 (n = 40, 42, 44) family by reacting 2-bromodiethyl malonate with NaH as the base. The observed reactivity trend was C80 > C84 > C88. For the C80 cage, both a mono-adduct and bis-adduct were isolated, for C84, only a mono-adduct was obtained, whereas for C88, no addition reaction was observed even when the reaction temperature was increased from room temperature to 60°C. The differences in reactivity were attributed to the strain and curvature of these cages, with C80 having the most strain and C88 the lowest.

**[2 + 2] cycloaddition reactions**

Cycloaddition reactions of the type [4 + 2], [3 + 2] and [2 + 1], which work well with empty fullerenes, have also been applied successfully to endohedral fullerenes. Very recently, our group was successful in the preparation of the first [2 + 2] cycloaddition mono-adduct of Sc3N@h-C80 from the reaction between benzene and the endohedral metallofullerene. Studies of the addition of benzene rings to fullerenes are known.

In the case of Gd@C82, the benzene addition occurs at both [5,6] and [6,6] bonds. In the case of Lu@C82, the addition of anthranilic acid and isoamyl nitride both occur at a [5,6]-ring junction. These observations lead to the question of whether the carbon cage or the encapsulated moiety dictates the regioselectivity addition pattern. We reported the synthesis, characterization, regioselective addition and properties of [2 + 2] cycloaddition reaction adducts, which had not been previously studied for trimetallic nitride endohedral metallofullerenes.

The addition of benzene to the least reactive TNT EMF Sc3N@h-C80 occurred at both [5,6] and [6,6] bonds, affording two very stable isomeric mono-adducts. This is the second example of Sc3N@h-C80 producing both isomers in the same reaction. Crystallographic data showed that both the Sc3N moiety and the cage are disordered in the [5,6] isomer, whereas for the [6,6] isomer, the fullerene cage is fully ordered. The Sc3N moiety adopts the usual planar geometry and is arranged so that the scandium atoms avoid interaction with the carbon atoms near the site of addition in both isomers (Fig. 11). This is the first time where the electrochemical behavior of a [6,6] mono-adduct isomer of Sc3N@h-C80 was studied, and surprisingly, it exhibits reversible cathodic behavior, which is typically not observed for the [6,6] adducts. The relatively high thermal stabilities of both isomeric mono-adducts suggest that this type of exohedral functionalizations can be employed for the preparation of new TNT EMFs derivatives for potential applications in the field of organic photovoltaic devices. It is important to note that the [5,6] and [6,6] isomers do not interconvert thermally, so both are intrinsically stable thermodynamically.

**Electrosynthesis of endohedral metallofullerenes**

The exohedral functionalization methodology used with endohedral metallofullerenes has been focused mainly on cycloaddition reactions, discussed in the previous sections. Therefore, it was of interest to explore new strategies for the functionalization of TNT EMFs, to expand their breadth and their possible potential applications.

![Figure 11](image-url)
Fullerene anions can be generated easily and quantitatively by chemical or electrochemical methods. Electrochemical methods provide excellent control over the state of reduction. Anionic empty fullerenes have been extensively studied as nucleophilic reagents for exohedral functionalization of the cages. However, nothing was known about the reactivity of anionic endohedral metallofullerenes until 2011 when our group reported the first derivative of Lu$_3$N@$_h$-C$_{80}$ prepared via the reaction of the dianion [Lu$_3$N@$_h$-C$_{80}$]$^{2-}$, obtained by controlled potential electrolysis (CPE), with benzal bromide (PhCHBr$_2$). The endohedral compound was reduced to the dianion in a solution of 0.05 M TBNPF$_6$/o-DCB:DMF as the supporting electrolyte under CPE at $-1.60 \text{ V}$ under an argon atmosphere. Addition of an excess of PhCHBr$_2$ afforded the desired mono-adduct derivative. $^1$H NMR studies suggested that the addition occurred exclusively at a [6,6] bond. Electrochemistry, UV–vis–NIR and NMR studies indicated that the derivative is most likely an open [6,6] regioisomer. Unfortunately, attempts to perform the same reaction with Sc$_3$N@$_h$-C$_{80}$ were not successful. To understand the differences in reactivity, DFT calculations were performed. The latter demonstrated that the HOMO of [Lu$_3$N@$_h$-C$_{80}$]$^{2-}$ contains substantial charge on the cage, whereas [Sc$_3$N@$_h$-C$_{80}$]$^{2-}$ has most of the charge localized on the cluster. Thus, [Lu$_3$N@$_h$-C$_{80}$]$^{2-}$ is more nucleophilic and therefore more reactive than [Sc$_3$N@$_h$-C$_{80}$]$^{2-}$.

Very recently, we were able to synthesize the first Sc$_3$N@$_h$-C$_{80}$ derivative by reacting the trianion, [Sc$_3$N@$_h$-C$_{80}$]$^{3-}$ with benzal bromide. The trianion was obtained under similar conditions as those used to prepare [Lu$_3$N@$_h$-C$_{80}$]$^{2-}$ but using a solution of 0.1M tetra-n-butylammonium perchlorate (n-Bu$_4$NClO$_4$) as the supporting electrolyte, and the potential was kept at $-2.10 \text{ V}$. As in the case of the Lu$_3$N@$_h$-C$_{80}$ derivative, NMR, UV–vis–NIR, electrochemistry and DFT calculations suggest that the formation occurred at a [6,6] bond and that it is an open-cage mono-adduct. Computational results revealed that the SOMO of [Sc$_3$N@$_h$-C$_{80}$]$^{3-}$ has substantial charge on the cage, whereas the HOMO of [Sc$_3$N@$_h$-C$_{80}$]$^{2-}$ is mainly localized on the cluster, explaining why the dianion of Sc$_3$N@$_h$-C$_{80}$ is not reactive enough towards nucleophilic reactions (Fig. 12).

There are several advantages of using the electrosynthetic method over the conventional ones to prepare similar compounds.

Those are as follows: (i) room temperature reactions; (ii) controlled addition of reagents to prevent the common and sometimes uncontrolled multiaddition of addends; and (iii) short reaction times. This method can be employed as a complement to the conventional methods for the exohedral functionalization of endohedral fullerenes.

### APPLICATIONS OF ENDOHEDRAL FULLERENES

Several applications of endohedral fullerenes have been explored widely because of the rich electronic properties of these compounds. Because the HOMO–LUMO gap depends on the encapsulated clusters, cage size, cage symmetry and exohedral functionalizations, the energy band gaps can be finely tuned for potential molecular electronic applications. As mentioned previously, applications in medicine have been exploited as well, where the inertness of the incarcerated moiety and the paramagnetic properties of some endohedral fullerenes make them attractive for magnetic resonance imaging applications.

Despite their rich electronic properties, only a few reports of the applications of endohedral fullerenes exist. Our group has worked and reported several donor-acceptor systems of endohedral fullerenes for potential applications in photovoltaic devices. Such results suggest that endohedral fullerenes, due to the possibility of finely tuning their molecular orbitals, are excellent candidates as electron acceptors in donor-acceptor systems.

### THEORETICAL STUDIES

Theoretical studies have played an important role in the understanding of endohedral fullerenes. Moreover, it has helped explain particular observations, such as reactivity and preferential templating of an encapsulated moiety with a particular carbon cage. It is known that the stabilization of a particular encapsulated cluster and fullerene cage is achieved by an electron transfer mechanism from the inner cluster to the cage. An ionic model has been proposed for endohedral metallofullerenes, and it has been widely accepted for the trimetallic nitride family. Chaur et al. studied the formal charge transfer from the metallic clusters to the fullerene.

![Figure 12](image-url) Electronic structures of anionic Sc$_3$N@$_h$-C$_{80}$ and anionic Lu$_3$N@$_h$-C$_{80}$ species with the most stable DFT optimized structures. “Reprinted with permission from Li et al., Journal of the American Chemical Society, 2012, 134, 7480. Copyright 2012 American Chemical Society”
cages through electrochemical experiments and theoretical studies for the large TNT EMF $M_2N_6@C_{2n}$ ($M=$La, Ce and Pr; $n=46, 48$).\cite{113} This study verified that the ionic model, $M_2N_6@C_{2n}$, applies well for the TNT EMFs that we studied. This model assumes that a formal charge transfer of six electrons from the metallic cluster to the fullerene cage fills the lowest three unoccupied molecular orbitals of the cage. Thus, the measured electrochemical band gaps are expected to correspond to the energy difference between LUMO + 3 and LUMO + 2. Figure 13 shows the excellent correlation found between the electrochemically measured solution HOMO – LUMO gaps and the theoretically calculated [(LUMO + 3) – (LUMO + 2)] values. Attempted correlations between the electrochemical gaps with [(LUMO + 1) – (LUMO – 1)] and [(LUMO + 2) – (LUMO + 1)], assuming two or four electron transfers from the cluster to the cage, respectively, were very poor. These results provide very strong experimental/theoretical support for the ionic model.\cite{113} A recent study by Wang and co-workers for $M_2N_6@C_{88}$ ($M=$La, Gd) clearly agrees with our results, which concluded that the formal charge transfer from the internal cluster to the fullerene cage determines the structure and stabilities of the parent cage.\cite{60}

\section*{OUTLOOK}

Endohedral fullerenes are very interesting compounds from the structural and fundamental point of view but mainly because of their rich electronic properties. Strong ionic interactions due to substantial charge transfer between the incarcerated cluster and the fullerene cages are important in determining the electronic properties and stabilities of these compounds. The ability to finely tune the HOMO – LUMO gaps of these compounds combined their electron-acceptor properties, and low reorganization energies upon electron transfer make them excellent candidates as electron-acceptor compounds for organic solar cell applications. Furthermore, exohedral functionalization has led to the preparation of donor-acceptor conjugates with long-lived charge separated states. Unfortunately, the low yield of these compounds continues to be an impediment in their use in organic photovoltaics.

Despite the many contributions by different research groups in the field of endohedral fullerenes, there are still many questions that remain unanswered. Incarcerating new clusters and increasing the yields are challenges that need to be overcome if these compounds are to find real applications in the future. Undoubtedly, the endohedral fullerene field is a fascinating and challenging area, where many new compounds with potential applications remain to be prepared and characterized. The interplay between the nature of the encapsulated cluster and the exohedral chemistry of these compounds is not only an interesting field of fundamental importance; it is relevant to the understanding of the properties of graphene. There are very few systems that allow the quantitative study of electronic interactions across a single layer of carbon atoms, as these endohedral fullerene compounds are able to do.

\section*{Acknowledgements}

The authors wish to thank the National Science Foundation, grants CHE-1110967 and CHE-1124075, for generous financial support as well as the Robert A. Welch Foundation for an endowed chair to L.E., grant #AH-0033.

\section*{REFERENCES}