

# Buckyball maracas: exploring the inside and outside properties of endohedral fullerenes<sup>†</sup>

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Since the experimental observation of the encapsulation of different species inside fullerene (endohedral fullerenes) cages, several research groups have focused their research in the elaboration of new and novel compounds. Exohedral functionalization of the carbon cages has helped in the discovery of new species and has expanded their potential applications in material science and medicine. Our research group has contributed to the discovery, functionalization, and characterization of new and interesting compounds that have been explored in different applications, but mainly in the field of organic photovoltaics. Here, we report the contribution and progress of our research group in the field of buckyball "maracas." Copyright © 2012 John Wiley & Sons, Ltd.

**Keywords:** electrochemistry; electronic properties; endohedral fullerenes

## INTRODUCTION

Since the discovery of the first endohedral fullerene, La@C<sub>60</sub>, in 1985 by Smalley *et al.*,<sup>[1]</sup> there has been increasing interest in the encapsulation of different species in hollow carbon cages. Advances in the entrapment of different species (such as inert rare gas atoms and diatomic molecules) inside fullerene cages, their isolation and characterization have been accomplished since then.<sup>[2–7]</sup>

The discovery of a trimetallic nitride template endohedral metallofullerene (TNT EMF) by Stevenson *et al.* in 1999 revolutionized the field with the isolation of the third most abundant fullerene that can be prepared to date (after C<sub>60</sub> and C<sub>70</sub>); Sc<sub>3</sub>N@C<sub>80</sub>.<sup>[8]</sup> With the introduction of nitrogen gas into a Krätschmer–Huffman arc generator, the yield of the Sc<sub>3</sub>N@C<sub>80</sub> product was significantly enhanced and exceeded the yields of empty-cage C<sub>84</sub> isomers. There has been much interest in M<sub>3</sub>N@C<sub>2n</sub> (*n* = 34–50) compounds because of their interesting chemical and physical properties, and the possible synthesis of many new metallic nitride families. The interest of encapsulating metals, metal clusters and other species has gone beyond simple curiosity because some have found potential applications in materials science and medicine. For instance, gadolinium EMFs have been studied as potential magnetic resonance imaging contrast-enhancing agents.<sup>[9–11]</sup> Furthermore, the electronic properties of EMFs, such as low HOMO – LUMO gaps, have made them potential targets for molecular electronic and photovoltaic applications, and in the design of new electron-donor/electron-acceptor molecular dyads and triads.<sup>[9,12–22]</sup> Endohedral fullerenes containing metallic carbides,<sup>[23–33]</sup> metallic oxides,<sup>[34–37]</sup> and metallic sulfides<sup>[38–40]</sup> are also known, as well as mixed nitride/carbides.<sup>[41]</sup>

The carbon atoms in fullerenes are arranged into 12 pentagons and a larger and variable number of hexagons, and the latter increases as the carbon cage size increases.<sup>[42]</sup> The most stable empty fullerenes are those that obey the isolated-pentagon rule (IPR), which states that all the pentagons in a fullerene cage are surrounded exclusively by hexagons to alleviate the strain produced when two pentagon rings are fused. There has not been a single exception to this rule for empty-cage fullerenes, but for

endohedral metallofullerenes, this rule seems to be more of a suggestion, because several non-IPR cages have been isolated and characterized.<sup>[28,40,43–51]</sup>

The chemical functionalization of endohedral fullerenes has expanded their potential applications and modified their chemical properties. The first derivative of an EMF was for La@C<sub>82</sub>, reported by Akasaka, *et al.*, and obtained from a photochemical reaction with disiliranes.<sup>[52]</sup> With the use of exohedral functionalization, new endohedral fullerenes have been identified because of the easier crystallization of the corresponding derivatives compared with the pristine cages.<sup>[25,44,53–55]</sup>

Herein, we report the contributions and progress of our research group in 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.

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## Biography

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## Biography

Julio R. Pinzón obtained his PhD in 2010 from Clemson University (Clemson, SC – USA). He currently holds a position as an Associate Professor at the Environmental Chemistry Department Universidad Santo Tomás (Bucaramanga, Colombia). His research interest is focused on the synthesis of fullerene-based D-A systems and organic dyes with potential application in molecular electronics and organic solar cells.



## Biography

Steven Stevenson received his BSc degree in Chemistry from Angelo State University in San Angelo, Texas in 1986. He received his MS degree (1992) in Chemistry and his PhD (1995) in Analytical Chemistry both from Virginia Tech. After an industrial appointment at Luna Innovations (2000–2004), Stevenson pursued an academic career at the University of Southern Mississippi (2004–2011) and in 2011 moved to his current institution (Indiana-Purdue University at Fort Wayne, IPFW). His research interests include the discovery, electric-arc synthesis, and separation science of metallofullerenes.



## Biography

Prof. Luis Echegoyen was born in La Habana, Cuba, in 1951. He obtained both his BSc and PhD from the University of Puerto Rico in Río Piedras (1971 and 1974, respectively). After an industrial placement at Union Carbide and several professorships at the Universities of Puerto Rico, Maryland, and Miami, in 2002 he was appointed as Chair of the Department of Chemistry at Clemson University, in South Carolina. Later, he served as Division Director for Chemistry at the National Science Foundation for 4 years (2006–2010), and more recently, he became the Robert A. Welch Professor of Chemistry at the University of Texas–El Paso in 2010. His research interests include fullerene chemistry, electrochemistry, and supramolecular chemistry, with special emphasis in photovoltaics and endohedral fullerenes.



## ENDOHEDRAL FULLERENES

## Trimetallic nitride endohedral fullerenes

Since the discovery of the high-yielding TNT EMF,  $Sc_3N@C_{80}$ , 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 ( $N_2$  or  $NH_3$ ) in a Krätschmer–Huffman arc reactor (Fig. 1).<sup>[8]</sup> 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  $M_3N@C_{2n}$  ( $38 \leq n \leq 44$ ) where the  $C_{80}$  cage is the most abundant because of charge transfer stabilization between the metal cluster and the carbon cage.<sup>[56]</sup> An interesting observation is that empty  $I_h$ - and  $D_{5h}$ - $C_{80}$  cages have never been isolated, nor has  $Sc_3N$  outside the carbon cages. Out of the seven possible constitutional isomers for  $C_{80}$  that obey the IPR rule, only the stable empty cages  $D_2$  and  $D_{5d}$  have been isolated.<sup>[57,58]</sup> On the other hand, the two least stable empty isomers,  $I_h$  and  $D_{5h}$ , are the predominant ones when encapsulating the metallic clusters. Along with the isolation of the most abundant  $M_3N@C_{80}$



Figure 1. Krätschmer–Huffman arc reactor in our research facilities

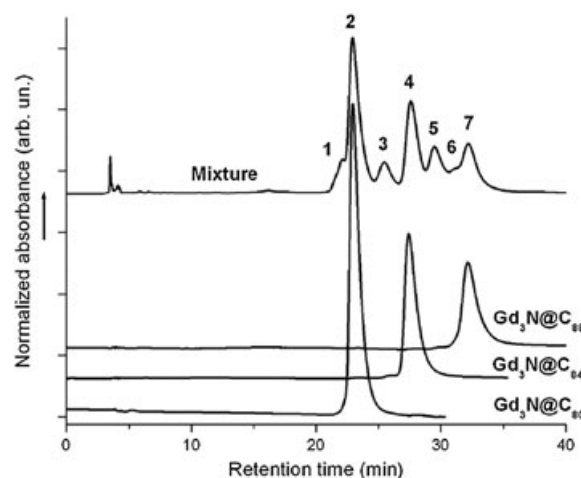
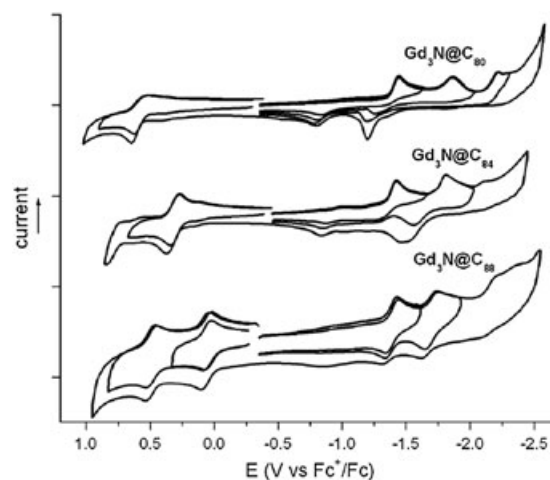


Figure 2. High-performance liquid chromatography chromatograms of the  $Gd_3N@C_{2n}$  mixtures and isolated products. “Reprinted with permission from Chaur *et al.*, *Journal of the American Chemical Society*, **2007**, 129, 47, 14826. Copyright 2007 American Chemical Society”

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.<sup>[25,31,49,51,54,59–64]</sup>

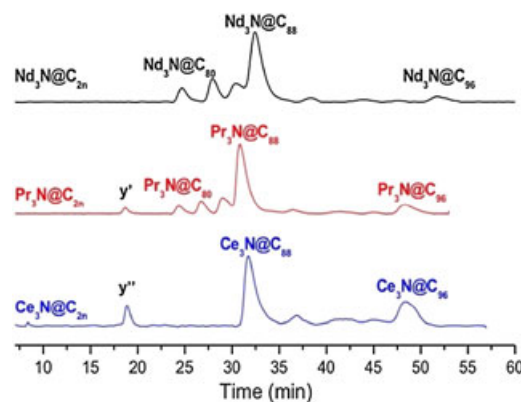
Higher metallic nitride endohedral fullerenes  $M_3N@C_{2n}$  ( $M = \text{La, Dy, Tm, Nd, Gd, Pr, Ce, Y}$ ;  $40 \leq n \leq 55$ ) have been studied extensively. Interestingly, their electrochemical behavior is different from those of the corresponding smaller cages. Our group reported the first electrochemical study of higher endohedral metallofullerenes and the first electrochemical studies for the gadolinium nitride endohedral fullerene family,  $Gd_3N@C_{2n}$  ( $n = 40, 42$  and  $44$ ).<sup>[64]</sup> This family spans from small cages such as  $C_{78}$  to larger ones, such as  $C_{88}$ . 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  $Gd_3N@C_{2n}$  ( $n = 40, 42, 44$ ), respectively. The UV–vis of these three EMFs indicates that the band gap for  $Gd_3N@C_{2n}$  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  $Gd_3N@C_{80}$ ,  $Gd_3N@C_{84}$  and  $Gd_3N@C_{88}$ .  $Gd_3N@C_{80}$  and  $Gd_3N@C_{84}$  exhibit similar electrochemical behavior, but  $Gd_3N@C_{88}$  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.<sup>[65]</sup>

In the TNT EMF families, the common preferential templating of the  $C_{80}$  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,  $C_{88}$ , in the case of  $Nd_3N@C_{2n}$  ( $40 \leq n \leq 49$ ).<sup>[63]</sup> 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  $C_{80}$  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.<sup>[61]</sup> As shown in Fig. 4, the preferentially templated cage is  $C_{88}$ , 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  $Ce_3N@C_{2n}$  family, in which  $Ce_3N@C_{96}$



**Figure 3.** Cyclic voltammograms of  $Gd_3N@C_{2n}$  ( $n = 40, 42, 44$ ) in 0.05 M of TBNPF<sub>6</sub>/o-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"

is the second most abundant species within the family. Later on, we found that in the case of the  $La_3N@C_{2n}$  family, the  $C_{96}$  cage predominates, and  $C_{88}$  is the second most abundant.<sup>[66]</sup> No  $C_{80}$



**Figure 4.** High-performance liquid chromatography chromatograms of the  $Nd_3N@C_{2n}$  (top),  $Pr_3N@C_{2n}$  (middle) and  $Ce_3N@C_{2n}$  (bottom) endohedral metallofullerene families.  $y'$ :  $Pr@C_{84}$ ,  $y''$ :  $Ce@C_{84}$ . Conditions: eluent = toluene, flow rate =  $4.0 \text{ ml min}^{-1}$ ; Buckyprep-M column; detection wavelength = 372 nm. "Reprinted (adapted) with permission from Chaur *et al.*, Chemistry – A European Journal, **2008**, 14, 459"

**Table 1.** UV–vis onset, band gaps and redox potentials for  $M_3N@C_{2n}$  ( $M = \text{Gd, Nd, Pr, Ce}$ ;  $n = 40, 42, 44$ ) endohedral families

TNT EMF	UV–vis onset (nm)	Band gap (eV) <sup>a</sup>	Redox potentials (V)					
			$E_{\text{ox}}^1$	$E_{\text{ox}}^2$	$E_{\text{red}}^1$	$E_{\text{red}}^2$	$E_{\text{red}}^3$	$\Delta E_{\text{gap}}$
$Gd_3N@C_{80}$	780	1.60	+0.58 <sup>b</sup>		–1.44	–1.86	–2.15	2.02
$Gd_3N@C_{84}$	1375	0.90	+0.32 <sup>b</sup>		–1.37	–1.76		1.69
$Gd_3N@C_{88}$	1495	0.83	+0.06 <sup>b</sup>	+0.49 <sup>b</sup>	–1.43 <sup>b</sup>	–1.38 <sup>b</sup>		1.49
$Nd_3N@C_{88}$	1420	0.87	+0.07 <sup>b</sup>		–1.33 <sup>b</sup>			1.40
$Pr_3N@C_{88}$	1445	0.86	+0.09 <sup>b</sup>		–1.31 <sup>b</sup>			1.40
$Ce_3N@C_{88}$	1442	0.86	+0.08 <sup>b</sup>		–1.30 <sup>b</sup>			1.38

TNT EMF, trimetallic nitride template endohedral metallofullerene.

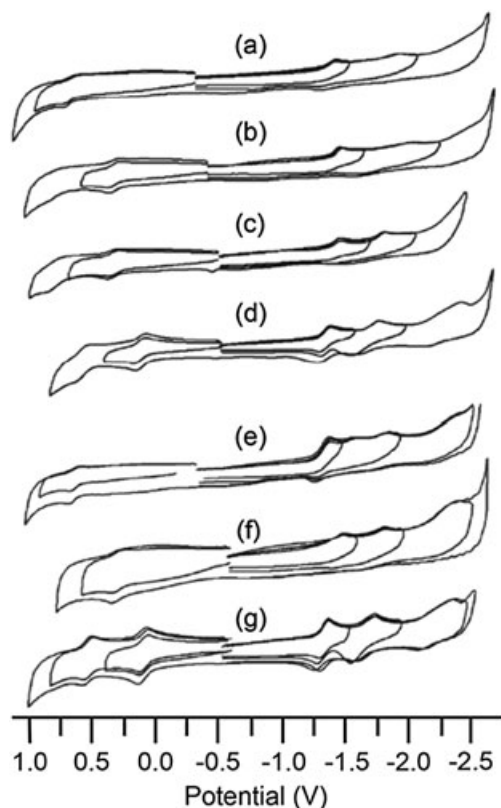
<sup>a</sup>Band gap calculated from the spectral onset; band gap (eV)  $\approx 1240/\text{onset (nm)}$ .

<sup>b</sup>Denotes half-wave potentials.

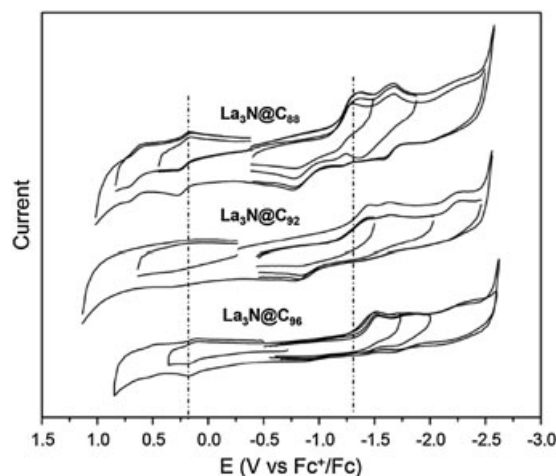


cage is observed for Ce or La. The electrochemical properties of these large EMFs families resulted in the observation of reversible reduction processes for the  $C_{88}$  cage but irreversible reduction processes for the smaller cage, and the oxidation potentials were lower for the larger cages (Fig. 5). These results are in agreement with the  $Gd_3N@C_{88}$  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.<sup>[65]</sup>

The question of whether higher metallic clusters can template higher fullerene cages,  $C_{2n}$  ( $n > 49$ ), was resolved by our group with the case of  $La_3N@C_{2n}$  ( $43 \leq n \leq 55$ ) family, which is the first report of the  $La_3N$  cluster encapsulated inside fullerene cages.<sup>[66]</sup> The  $C_{96}$  cage predominates for the  $La_3N$  cluster. The  $La_3N@C_{2n}$  family is composed of fullerene cages as low as  $C_{88}$  and as high as  $C_{104}$  from which only three fractions were isolated and purified, and identified by MALDI-TOF MS as  $La_3N@C_{88}$ ,  $La_3N@C_{92}$  and  $La_3N@C_{96}$ . The observed trend leads to the prediction that the next preferentially templated cages, if larger metals are used, would be the  $C_{104}$  cage. Interestingly, as the metal size increases, preferential templating goes from the  $C_{80}$  cage to  $C_{88}$ , the  $C_{96}$  and apparently  $C_{104}$  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  $M_3N@C_{88}$  is reversible in both reductive and oxidative scans.<sup>[63,64]</sup> Interestingly, this behavior was not observed for  $La_3N@C_{2n}$  ( $44 \leq n \leq 48$ ),  $La_3N@C_{88}$  exhibits irreversible oxidation



**Figure 5.** Cyclic voltammograms of (a)  $Nd_3N@C_{80}$ , (b)  $Nd_3N@C_{84}$ , (c)  $Nd_3N@C_{86}$ , (d)  $Nd_3N@C_{88}$ , (e)  $Pr_3N@C_{80}$ , (f)  $Pr_3N@C_{86}$  and (g)  $Pr_3N@C_{88}$  in 0.05 M TBPNE<sub>4</sub>/o-DCB solution versus the internal reference redox couple ferrocene/ferrocenium at a scan rate of 100 mV/s. "Reprinted (adapted) with permission from Chaur *et al.*, Chemistry – A European Journal, **2008**, 14, 4594"



**Figure 6.** Cyclic voltammograms of  $La_3N@C_{88}$ ,  $La_3N@C_{92}$  and  $La_3N@C_{96}$  in 0.05 M TBPNE<sub>4</sub>/o-DCB solution versus the internal reference redox couple ferrocene/ferrocenium at a scan rate of 100 mV/s. "Reprinted with permission from Chaur *et al.*, Chemistry – A European Journal, **2008**, 14, 8213"

and reduction steps unlike the other  $M_3N@C_{88}$  (Fig. 6 and Table 1). On the other hand,  $La_3N@C_{92}$  and  $La_3N@C_{96}$  exhibit similar electrochemistry and HOMO – LUMO gaps.

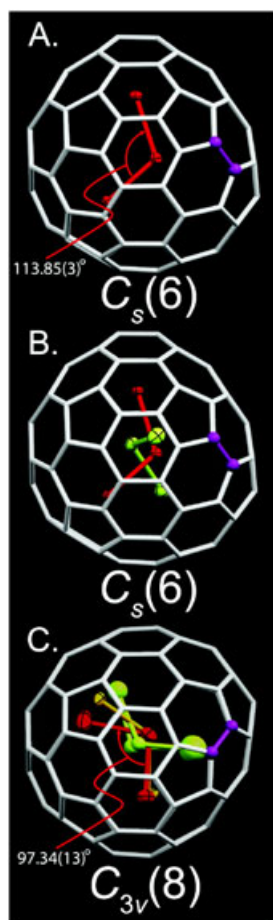
#### Metallic sulfide endohedral fullerenes

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 fullerenes  $M_2S@C_{82}$  ( $M = Sc, Y, Dy$  and  $Lu$ ) using  $CH_3N_3 \cdot HSCN$  as a solid sulfur source.<sup>[38]</sup> The only  $M_2S@C_{82}$  cage isomer observed was determined to be the IPR ( $C_{3v}$ :8).

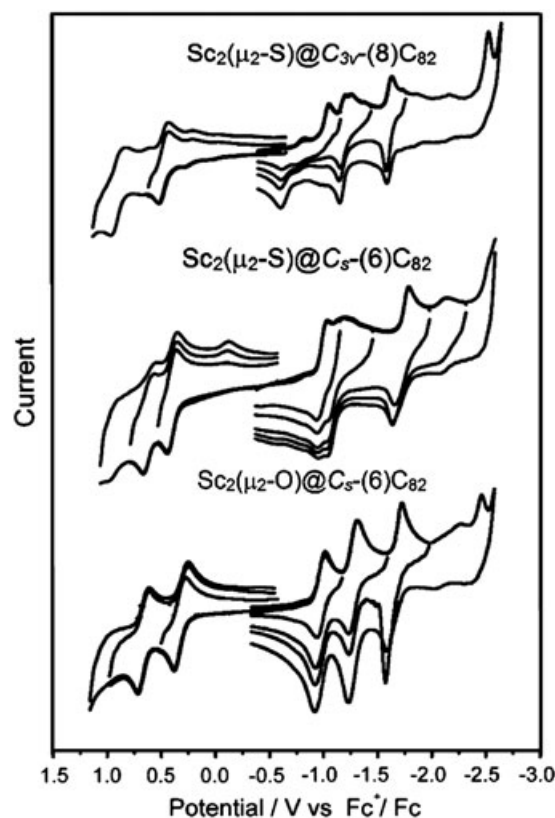
Recently, our group reported the synthesis of the extended endohedral fullerene family,  $Sc_2S@C_{2n}$  ( $n = 40–50$ ) in macroscopic quantities by the introduction of  $SO_2$  instead of a solid compound as the sulfur source.<sup>[39]</sup> Two different high-performance liquid chromatography (HPLC) fractions contain  $Sc_2S@C_{82}$  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  $Sc_2S@C_{82}$  ( $C_{3v}$ :8) and a new isomer  $Sc_2S@C_{82}$  were identified as the most abundant species within the family. It is known that electronic absorption of metallofullerenes is due to  $\pi-\pi^*$  transitions of the fullerene cage; thus, correlations between the cage symmetry and the UV-vis absorptions are easily established.<sup>[4,67]</sup> The UV-Vis-NIR spectra of both isomers showed that one of them was the reported  $C_{3v}$ :8, whereas the other was assigned as the  $C_5$ :6 cage based on spectroscopic similarities with those of the previously reported  $Y_2C_2@C_{82}$ .<sup>[24]</sup> 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.<sup>[38]</sup> Prior studies with empty IPR  $C_{82}$  and  $C_{82}^{4-}$  fullerenes have shown that isomer 8 with  $C_{3v}$  symmetry is the lowest energy species when the fullerene has a 4- charge electron. On the other hand, isomers  $C_{2v}$ :9 and  $C_5$ :6 are the second and third lowest energy species.<sup>[29]</sup> After encapsulation of the  $Sc_2S$  moiety, the experimentally observed  $C_{3v}$ :8 and  $C_5$ :6 isomers have similar stabilities, in agreement with the isolation of the two isomers.

The two  $Sc_2S@C_{82}$  isomeric cages were confirmed by X-ray crystallography by Mercado *et al.*, and electrochemical and computational studies were reported.<sup>[68]</sup> The crystallographic

studies revealed that both isomers contain fully ordered carbon cages. Additionally,  $\text{Sc}_2(\mu_2\text{-S})@C_5(6)\text{-C}_{82}$  revealed two slightly different cage sites and a fully ordered  $\text{Sc}_2\text{S}$  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 Sc-S-Sc angles in  $\text{Sc}_2(\mu_2\text{-S})@C_5(6)\text{-C}_{82}$  and  $\text{Sc}_2(\mu_2\text{-S})@C_{3v}(8)\text{-C}_{82}$  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  $C_5:6$ ) is significantly different,  $\text{Sc}_2(\mu_2\text{-S})@C_5(6)\text{-C}_{82}$  exhibits an almost reversible first reduction potential, whereas the one for  $\text{Sc}_2(\mu_2\text{-S})@C_{3v}(8)\text{-C}_{82}$  is completely irreversible, but a well-defined fourth reduction peak not observed for the  $\text{Sc}_2(\mu_2\text{-S})@C_5(6)\text{-C}_{82}$  is observed for the  $\text{Sc}_2(\mu_2\text{-S})@C_{3v}(8)\text{-C}_{82}$  isomer (Fig. 8). The differences in the electrochemical behavior are more pronounced for the oxidation processes. The oxidation peaks



**Figure 7.** The two  $\text{Sc}_2(\mu_2\text{-S})@C_{82}$  isomers arranged with their mirror planes parallel to the page. (A) The internally ordered fullerene site A in the asymmetric unit of and  $\text{Sc}_2(\mu_2\text{-S})@C_5(6)\text{-C}_{82}\text{Ni}^{\text{II}}(\text{OEP})_2\text{C}_6\text{H}_6$ . The  $\text{Sc}_2(\mu_2\text{-S})$  unit is shown in red. (B) The internally disordered fullerene site B in  $\text{Sc}_2(\mu_2\text{-S})@C_5(6)\text{-C}_{82}$ . The  $\text{Sc}_2(\mu_2\text{-S})$  unit is modeled with the major site shown in red [fractional occupancy 0.826(2)] and the minor site shown in yellow-green [fractional occupancy 0.174(2)]. (C) The internally disordered fullerene site in  $\text{Sc}_2(\mu_2\text{-S})@C_{3v}(8)\text{-C}_{82}$ . The  $\text{Sc}_2(\mu_2\text{-S})$  portion is disordered and modeled in four positions. Note the decrease in the Sc-S-Sc angle between A and C labeled in white. "Reprinted with permission from Mercado *et al.*, Journal of the American Chemical Society, **2011**, 133, 17, 6752. Copyright 2011 American Chemical Society"



**Figure 8.** Cyclic voltammograms of  $\text{Sc}_2(\mu_2\text{-S})@C_5(6)\text{-C}_{82}$ ,  $\text{Sc}_2(\mu_2\text{-S})@C_{3v}(8)\text{-C}_{82}$  and  $\text{Sc}_2(\mu_2\text{-O})@C_5(6)\text{-C}_{82}$  in TBNPF<sub>6</sub>/o-DCB with ferrocene as the internal standard. Scan rate of 100 mV/s. "Reprinted with permission from Mercado *et al.*, Journal of the American Chemical Society, **2011**, 133, 17, 6752. Copyright 2011 American Chemical Society"

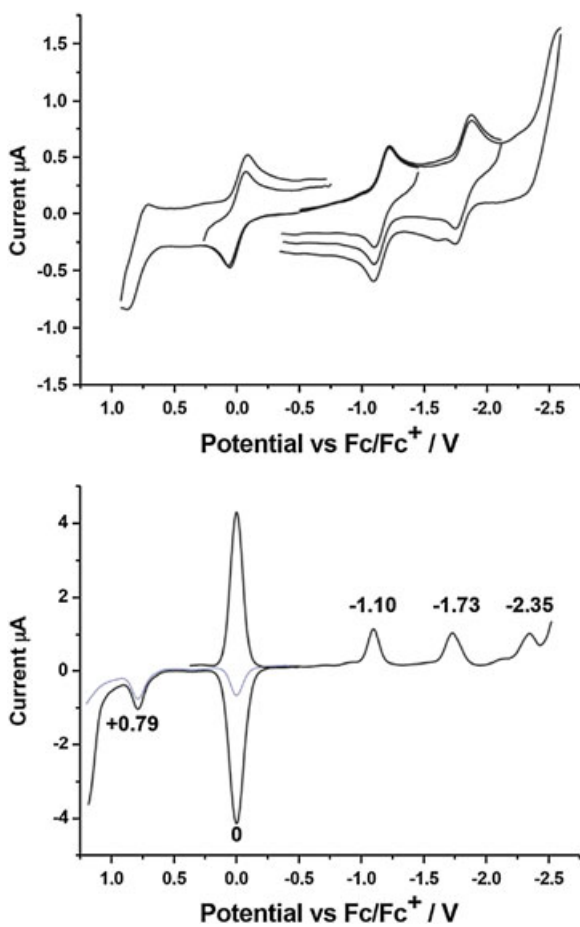
for the  $\text{Sc}_2(\mu_2\text{-S})@C_{3v}(8)\text{-C}_{82}$  are dramatically shifted anodically with respect to those for the  $\text{Sc}_2(\mu_2\text{-S})@C_5(6)\text{-C}_{82}$  isomer. This shows a remarkable difference in their HOMO orbital energies that can be related to the different electronic structures. A comparative study was carried out between  $\text{Sc}_2(\mu_2\text{-S})@C_5(6)\text{-C}_{82}$  and  $\text{Sc}_2(\mu_2\text{-O})@C_5(6)\text{-C}_{82}$ , 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).<sup>[40]</sup> This dimetallic sulfide cluster in a  $C_{72}$  cage,  $\text{Sc}_2\text{S}@C_{72}$ , was assigned to the  $C_5:10528$  symmetry on the basis of crystallographic analysis. Computational studies confirmed that a formal charge transfer of four electrons from the encapsulated moiety,  $\text{Sc}_2\text{S}$ , to the fullerene cage occurs in  $[\text{Sc}_2\text{S}]^{4+}@[\text{C}_{72}]^{4-}$ .<sup>[37,68]</sup> <sup>45</sup>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,  $\text{Sc}_2(\mu_2\text{-S})@C_5(6)\text{-C}_{82}$  and  $\text{Sc}_2(\mu_2\text{-S})@C_{3v}(8)\text{-C}_{82}$ . The reductive scan for  $\text{Sc}_2(\mu_2\text{-S})@C_5(10528)\text{-C}_{72}$  is reversible, 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  $\text{Sc}_4(\mu_3\text{-O})_2@I_h\text{-C}_{80}$ .<sup>[34]</sup> There is only one example of an electrochemical study of a metallic oxide endohedral fullerene, that is the case of  $\text{Sc}_2(\mu_2\text{-O})@C_5(6)\text{-C}_{82}$ .<sup>[37,68]</sup> We recently recorded the electrochemical behavior of  $\text{Sc}_4\text{O}_2@I_h\text{-C}_{80}$ , 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  $I_h\text{-C}_{80}$  based compounds (Fig. 9). The OSWV experiment shows three reductions with a separation of approximately 0.63 V. This is also different from  $C_{80}$  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,  $\text{Fc}/\text{Fc}^+$ , 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.



**Figure 9.** Cyclic Voltammogram (top) and Osteryoung Square Wave Voltammetry (bottom) of  $\text{Sc}_4\text{O}_2@I_h\text{-C}_{80}$  in 0.05 M TBNPF<sub>6</sub>/o-DCB with ferrocene as internal reference at a scan rate of 100 mV/s

### 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 nitride and metallic sulfide endohedral fullerenes. The egg-shaped endohedral fullerene  $\text{Gd}_3\text{N}@C_5(39663)\text{-C}_{82}$  is one of the two isomers previously predicted by computational studies to be stable for a  $C_{82}$  cage with a 6- charge electron.<sup>[49,69,70]</sup> X-ray crystallography showed a planar  $\text{Gd}_3\text{N}$  cluster unit, where one of the gadolinium ions is pointing directly to the vicinal pentalene 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  $\text{Tm}_3\text{N}@C_5(51365)\text{-C}_{84}$  and  $\text{Gd}_3\text{N}@C_5(51365)\text{-C}_{84}$ .<sup>[51]</sup> These endohedral fullerenes utilize the same cage symmetry ( $C_5$ ) of the previously reported  $\text{Tb}_3\text{N}@C_5(51365)\text{-C}_{84}$ , suggesting that it is the electron transfer from the cluster to the cage, rather than the nature of the encapsulated metallic nitride cluster that dictates the preferential templating of a particular cage, as noted from computational studies.<sup>[56,70]</sup> As in the case of  $\text{Gd}_3\text{N}@C_5(39663)\text{-C}_{82}$ , the internal cluster adopts a planar geometry, where one thulium atom in  $\text{Tm}_3\text{N}@C_5(51365)\text{-C}_{84}$  and one gadolinium atom in  $\text{Gd}_3\text{N}@C_5(51365)\text{-C}_{84}$  is pointing directly to the pentagon–pentagon fusion.

The first structural study of the non-IPR  $\text{Gd}_3\text{N}@C_2(22010)\text{-C}_{78}$  isomer by X-ray crystallography was also reported by our group.<sup>[71]</sup> Several endohedral fullerenes with a  $C_{78}$  cage had been structurally studied, but the majority possess a  $D_{3h}(5)\text{-C}_{78}$  cage symmetry.<sup>[72–76]</sup> 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  $\text{Gd}_3\text{N}$  in such a small cage is an interesting feature of this metallic nitride 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).

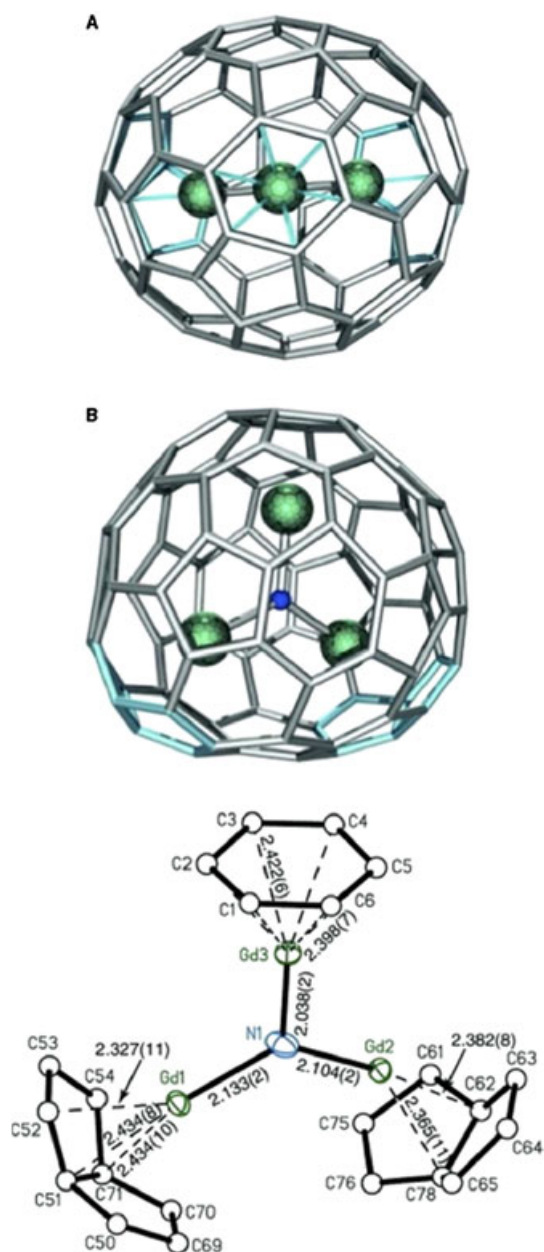
As previously discussed, our group reported the first non-IPR dimetallic sulfide cluster endohedral fullerene,  $\text{Sc}_2\text{S}@C_5(10528)\text{-C}_{72}$ . As for all non-IPR endohedral fullerene cages, the scandium ions were found to point to the vicinal pentalene units, which is a permanent characteristic 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





**Figure 10.** (Top) Two orthogonal views of  $Gd_3N@C_2(22010)-C_{78}$  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  $Gd_3N$  unit relative to the nearest carbon atoms of the fullerene cage in  $Gd_3N@C_2(22010)-C_{78}$ . 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"

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 adduct of  $Sc_3N@I_h-C_{80}$  and  $Y_3N@I_h-C_{80}$ .<sup>[77,78]</sup> The pyrrolidine adduct of

$Sc_3N@I_h-C_{80}$  was synthesized by means of the addition of an excess of *N*-ethylglycine and enriched  $^{13}C$ -paraformaldehyde in refluxing *o*-DCB. The corresponding fulleropyrrolidine *mono*-adduct was purified by column chromatography and characterized by different NMR techniques, such as,  $^1H$ ,  $^{13}C$  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  $I_h-C_{80}$  cage reported by Dorn and co-workers.<sup>[79,80]</sup>

Later in 2005, our research group reported the first pyrrolidine derivative of  $Y_3N@I_h-C_{80}$ .<sup>[78]</sup> In this case, the addition of the pyrrolidine adduct under identical conditions as those reported for the  $Sc_3N@I_h-C_{80}$  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- $M_3N@I_h-C_{80}$  ( $M = Y, Er$ ) was reported by our group as well.<sup>[81]</sup> Thus, the [6,6] isomer is the kinetic product in the case of  $Y_3N@I_h-C_{80}$ , whereas the [5,6] isomer is the thermodynamic product for both  $Y_3N@I_h-C_{80}$  and  $Sc_3N@I_h-C_{80}$ . 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.<sup>[82–84]</sup> The access to different malonic acid derivatives makes this approach a simple method for preparing different adducts. Attempts to perform this reaction on  $M_3N@I_h-C_{80}$  ( $M = Y, Er$ ) succeeded in our group and afforded the first mono-methanofullerene derivatives.<sup>[78,81]</sup> 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  $Y_3N@I_h-C_{80}$  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.<sup>[85]</sup> Attempts to perform this reaction under the same conditions with  $Sc_3$



**Scheme 1.** Cyclopropanation reaction of  $Y_3N@I_h-C_{80}$  with 2-bromodiphenyl malonate. X-Ray structure of product is shown. "Reprinted (adapted) with permission from Lukoyanova *et al.*, *Journal of the American Chemical Society*, **2007**, 129, 34, 10423. Copyright 2007 American Chemical Society"

$N@I_h-C_{80}$  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  $Sc_3N@I_h-C_{80}$  and  $Lu_3N@I_h-C_{80}$  in high yields using relatively typical conditions.<sup>[86]</sup> 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 adducts in high yields without the necessity of generating intermediate radicals that have been used by others.<sup>[87]</sup> An interesting observation was the reaction of 2,2-dibromodiethyl malonate, which resulted in identical results as with 2-bromodiethyl malonate. This is a remarkable result, because both 2-bromo and 2,2-dibromo malonates can react with fullerene cages if NaH is used as the base. 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  $Gd_3N@C_{2n}$  ( $n = 40, 42, 44$ ) family by reacting 2-bromodiethyl malonate in the presence of 1,8-diazobicycloundec-7-ene (DBU) as the base.<sup>[62]</sup> The observed reactivity trend was  $C_{80} > C_{84} > C_{88}$ . For the  $C_{80}$  cage, both a *mono*-adduct and *bis*-adduct were isolated, for  $C_{84}$ , only a *mono*-adduct was obtained, whereas for  $C_{88}$ , 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  $C_{80}$  having the most strain and  $C_{88}$  the lowest.

#### [2 + 2] cycloaddition reactions

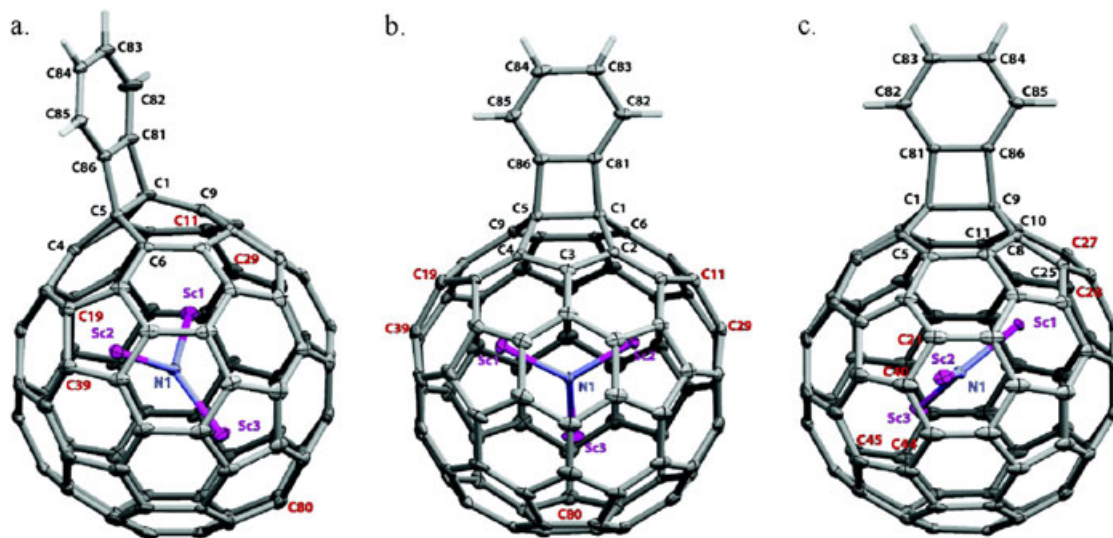
Cycloaddition reactions of the type [4 + 2], [3 + 2] and [2 + 1], which work well with empty fullerenes, have also been applied successfully to endohedral fullerenes. Very recently, our group was successful in the preparation of the first [2 + 2] cycloaddition *mono*-adduct of  $Sc_3N@I_h-C_{80}$  from the reaction between benzyne and the endohedral metallofullerene.<sup>[88]</sup> Studies of the addition of benzyne rings to fullerenes are known.<sup>[89–94]</sup>

In the case of  $Gd@C_{82}$ , the benzyne addition occurs at both [5,6] and [6,6] bonds.<sup>[93]</sup> In the case of  $La@C_{82}$ , the addition of anthranilic acid and isoamyl nitride both occur at a [5,6]-ring junction.<sup>[94]</sup> 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 benzyne to the least reactive TNT EMF  $Sc_3N@I_h-C_{80}$  occurred at both [5,6] and [6,6] bonds, affording two very stable isomeric *mono*-adducts. This is the second example of  $Sc_3N@I_h-C_{80}$  producing both isomers in the same reaction. Crystallographic data showed that both the  $Sc_3N$  moiety and the cage are disordered in the [5,6] isomer, whereas for the [6,6] isomer, the fullerene cage is fully ordered. The  $Sc_3N$  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  $Sc_3N@I_h-C_{80}$  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.** X-ray crystal structures of the [5,6]-benzyne mono-adduct (shown in two perspectives (a, b)) in crystalline  $Sc_3N@I_h-C_{80}(C_6H_4)_2CS_2$  ([5,6] isomer) and [6,6] benzyne mono-adduct (c) in crystalline  $Sc_3N@I_h-C_{80}(C_6H_4)_2CS_2$  ([6,6] isomer) drawn with 50% thermal contours. The carbon atoms closest to the scandium atoms are numbered in red. "Reprinted with permission from Mercado *et al.*, Journal of the American Chemical Society, 2011, 133, 1563. Copyright 2011 American Chemical Society"



Fullerene anions can be generated easily and quantitatively by chemical or electrochemical methods.<sup>[95,96]</sup> 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.<sup>[97–106]</sup> However, nothing was known about the reactivity of anionic endohedral metallofullerenes until 2011 when our group reported the first derivative of  $\text{Lu}_3\text{N}@I_h\text{-C}_{80}$  prepared via the reaction of the dianion  $[\text{Lu}_3\text{N}@I_h\text{-C}_{80}]^{2-}$ , obtained by controlled potential electrolysis (CPE), with benzal bromide ( $\text{PhCHBr}_2$ ).<sup>[107]</sup> The endohedral compound was reduced to the dianion in a solution of 0.05 M TBNPF<sub>6</sub>/o-DCB:DMF as the supporting electrolyte under CPE at  $-1.60\text{ V}$  under an argon atmosphere. Addition of an excess of  $\text{PhCHBr}_2$  afforded the desired *mono*-adduct derivative. <sup>1</sup>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  $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$  were not successful. To understand the differences in reactivity, DFT calculations were performed. The latter demonstrated that the HOMO of  $[\text{Lu}_3\text{N}@I_h\text{-C}_{80}]^{2-}$  contains substantial charge on the cage, whereas  $[\text{Sc}_3\text{N}@I_h\text{-C}_{80}]^{2-}$  has most of the charge localized on the cluster. Thus,  $[\text{Lu}_3\text{N}@I_h\text{-C}_{80}]^{2-}$  is more nucleophilic and therefore more reactive than  $[\text{Sc}_3\text{N}@I_h\text{-C}_{80}]^{2-}$ .

Very recently, we were able to synthesize the first  $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$  derivative by reacting the trianion,  $[\text{Sc}_3\text{N}@I_h\text{-C}_{80}]^{3-}$  with benzal bromide.<sup>[108]</sup> The trianion was obtained under similar conditions as those used to prepare  $[\text{Lu}_3\text{N}@I_h\text{-C}_{80}]^{2-}$  but using a solution of 0.1M tetra-*n*-butylammonium perchlorate ( $n\text{-Bu}_4\text{NClO}_4$ ) as the supporting electrolyte, and the potential was kept at  $-2.10\text{ V}$ . As in the case of the  $\text{Lu}_3\text{N}@I_h\text{-C}_{80}$  derivative, NMR, UV-vis-NIR, electrochemistry and DFT calculations suggest that the addition occurred at a [6,6] bond and that it is an open-cage *mono*-adduct. Computational results revealed that the SOMO of  $[\text{Sc}_3\text{N}@I_h\text{-C}_{80}]^{3-}$  has substantial charge on the cage, whereas the HOMO of  $[\text{Sc}_3\text{N}@I_h\text{-C}_{80}]^{2-}$  is mainly localized on the cluster, explaining why the dianion of  $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$  is not reactive enough towards nucleophilic reactions (Fig. 12).

There are several advantages of using the electrochemical 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 compliment to the conventional methods for the exohedral functionalization of endohedral fullerenes.

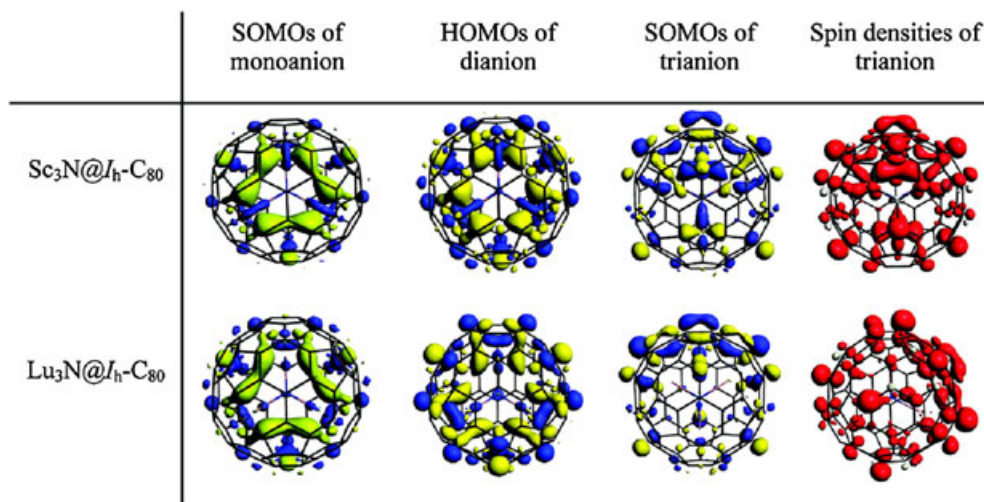
## APPLICATIONS OF ENDOHEDRAL FULLERENES

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.<sup>[9–11]</sup>

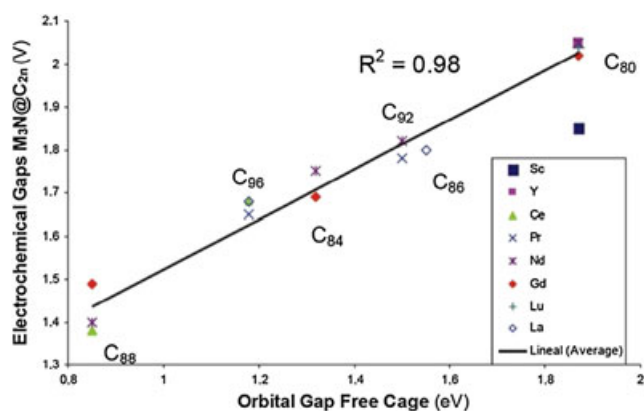
Despite their rich electronic properties, only a few reports of the applications of endohedral fullerenes exist.<sup>[12,14,16,17,21,109–111]</sup> Our group has worked and reported several donor-acceptor systems of endohedral fullerenes for potential applications in photovoltaic devices.<sup>[18–20,22,86]</sup> 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.<sup>[56,70,73,112]</sup> Chaur *et al.* studied the formal charge transfer from the metallic clusters to the fullerene



**Figure 12.** Electronic structures of anionic  $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$  and anionic  $\text{Lu}_3\text{N}@I_h\text{-C}_{80}$  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”



**Figure 13.** Correlation between electrochemical gaps and [(LUMO + 3) – (LUMO + 2)] orbital gaps in free carbon cages

cages through electrochemical experiments and theoretical studies for the large TNT EMF  $M_3N@C_{2n}$  ( $M = La, Ce$  and  $Pr$ ;  $n = 46, 48$ ).<sup>[113]</sup> This study verified that the ionic model,  $M_3N^{6+}@C_{2n}^{6-}$ , 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.<sup>[113]</sup> A recent study by Wang and co-workers for  $M_3N@C_{88}$  ( $M = La, Gd$ ) 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.<sup>[60]</sup>

## 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.

## Acknowledgements

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