

Review article

Endohedral fullerenes: Synthesis, isolation, *mono*- and *bis*-functionalizationMaira R. Cerón^{a,b,*}, Viviana Maffei^{a,c,d}, Steven Stevenson^e, Luis Echegoyen^{a,*}^a Department of Chemistry, University of Texas at El Paso, 500 West University Ave., El Paso, TX 79968, United States^b Physical and Life Sciences, Lawrence Livermore National Laboratory, 7000 East Ave. L-367, Livermore, CA 94550, United States^c Nano Carbon Materials Laboratory, Istituto Italiano di Tecnologia, Via Morego 30, Genova 16163, Italy^d Department of Chemistry and Industrial Chemistry, University of Genova, Via Dodecaneso 31, Genova 16146, Italy^e Department of Chemistry, Indiana-Purdue University at Fort Wayne, 2101 East Coliseum Boulevard, Fort Wayne, IN 46805, United States

ARTICLE INFO

Article history:

Received 17 February 2017

Received in revised form 26 March 2017

Accepted 27 March 2017

Available online 29 March 2017

Special Volume: Protagonists in Chemistry

Dedicated to Professor Luis Echegoyen

ABSTRACT

Here we present a short overview of the contribution of our research group to the discovery, functionalization and characterization of unprecedented endohedral fullerenes. We also report a comprehensive study of regioselective *bis*-1,3-dipolar cycloadditions to cluster endohedral fullerenes $M_3N@I_h-C_{80}$ ($M = \text{Lu}, \text{Y}$ and Er) and the spectroscopic characterization of the new *bis*-adducts obtained.

Published by Elsevier B.V.

Contents

1. Introduction	16
2. Synthesis, purification and characterization of endohedral fullerenes	17
3. Functionalization of endohedral fullerenes	18
3.1. 1,3-Dipolar cycloaddition	18
3.2. Bingel-Hirsch cyclopropanation	19
3.3. Electrosynthesis and [3+2] cycloaddition	19
4. Bis-1,3-dipolar cycloaddition of $M_3N@I_h-C_{80}$ ($M = \text{Lu}, \text{Y}$ and Er)	20
4.1. $M_3N@I_h-C_{80}$ ($M = \text{Lu}, \text{Y}$ and Er) Bisadducts characterization	20
4.2. Purification of $\text{Lu}_3N@I_h-C_{80}$ and $\text{Er}_3N@I_h-C_{80}$ using chemical methods	23
5. Conclusion	23
Acknowledgments	24
Appendix A. Supplementary data	24
References	24

1. Introduction

Fullerenes were discovered in 1985 by Kroto and co-workers as new carbon allotropes [1]. The investigation of their properties, reactivity and applications was not possible until macroscopic

quantities were available in 1990 [2]. In 1992, Echegoyen *et al.* reported the electrochemical detection of $C_{60}^{\bullet-}$ and $C_{70}^{\bullet-}$, and this manuscript became a very influential work in the field, cited 941 times [3]. Before getting involved in the endohedral fullerenes (EFs) field, Professor Echegoyen contributed to the electrochemical characterization of higher empty fullerenes [4–6], and to the *mono*- and *bis*-functionalization of C_{60} and C_{70} [7–14]. He was also the first to report a new route for the selective synthesis of [6,6]-methanofullerenes [15] and the useful *retro*-Bingel strategy to selectively protect-deprotect fullerene derivatives [9,16–21].

* Corresponding authors at: Physical and Life Sciences, Lawrence Livermore National Laboratory, 7000 East Ave. L-367, Livermore, CA 94550, United States (M.R. Cerón), University of Texas at El Paso, 500 West University Ave., El Paso, TX 79968, United States (L. Echegoyen)

E-mail addresses: ceronhernand1@llnl.gov (M.R. Cerón), echegoyen@utep.edu (L. Echegoyen).

2. Synthesis, purification and characterization of endohedral fullerenes

Endohedral fullerenes were reported soon after the discovery of C_{60} [22,23], but their low synthetic yields and inefficient separation methods limited the ability to fully investigate their properties. In 1999, Dorn *et al.* serendipitously revolutionized the endohedral fullerene field, with the discovery of the first cluster endohedral fullerene, $Sc_3N@I_h-C_{80}$ [24]. To date, $Sc_3N@I_h-C_{80}$, remains the most abundant endohedral fullerene and the third most abundant fullerene after C_{60} and C_{70} . Since the discovery of $Sc_3N@I_h-C_{80}$ many other nitride cluster fullerenes have been reported including scandium, yttrium and most of the lanthanides except Promethium, identifying cages ranging from C_{68} to C_{96} [25–31]. Numerous efforts have been made to improve the yields and separation of EFs, by either changing the arcing conditions or by using non-chromatographic methods to isolate targeted EFs [29]. Some of the alternative isolation methods are selective extraction [32–34], sublimation enrichment [35,36] and chemical reactions [37–40]. A specific example of a chemical-based separation method will be presented later. Echegoyen *et al.* developed an alternative method based on the differences of the oxidation potentials of EFs [41]. By selective chemical oxidation with acetylferrocenium $[Fe(COCH_3C_5H_4)Cp]^+$, Echegoyen and co-workers were able to isolate every member of the $Sc_3N@C_{2n}$ ($n = 34, 39$ and 40) family, with the advantage of separating large quantities of $Sc_3N@I_h-C_{80}$ after a single step [38,42,43].

Endohedral fullerenes are divided into two large groups, those that obey the isolated pentagon rule (IPR) and those that possess fused five-membered rings, or pentalene units (non-IPR) [44]. The isolated pentagon rule states that five-membered rings are always adjacent to six-membered rings. EFs that do not obey the IPR are fascinating to study because despite the large number of

possible non-IPR isomers, on the order of tens of thousands, frequently only one provides the perfect match for the encapsulated cluster. Here we present some of the exceptional examples of non-IPR EFs recently reported [45–47]. To date, five different types of junctions for IPR and non-IPR endohedral fullerenes have been reported, such as [5,5], [5,6], [6,6], [5,7] and [6,7] [48,49]. There are eighteen different types of possible C–C bonds of which thirteen have been experimentally observed [50–54] and two proposed by DFT calculations [55] (Fig. 1).

The Krätschmer–Huffman arcing synthesis is the method that has led to the discovery of unique EFs by changing the metal oxides/graphite powder mixture, discharge current, solid additives or the gases used in the reactor [56–59]. Echegoyen *et al.* contributed to the discovery of notable EFs such as the $Gd_3N@C_{2n}$ ($n = 39–43$) family [26,60–62], for which the existence of IPR exceptions is a common observation. The smallest cage member of the family ($Gd_3N@C_{2(22,010)}-C_{78}$) exhibits two pentalene units, while for larger cage members ($Gd_3N@C_{3(39,663)}-C_{82}$ and $Gd_3N@C_{3(51,365)}-C_{84}$) only one pentalene unit is observed [63]. Furthermore, for $Gd_3N@D_{3(17)}-C_{86}$ and $Gd_3N@D_{2(35)}-C_{88}$, which are the largest isolated members of the family, the cluster fits perfectly well without pyramidalization, and no pentalene units are observed (Fig. 2) [45,60,64].

By introducing SO_2 as a sulfur source, Echegoyen *et al.* were able to synthesize macroscopic quantities of a new family of EFs, $Sc_2S@C_{2n}$ ($n = 35–50$) [66]. Interestingly, changing the source of sulfur from guanidium thiocyanate ($CH_3N_3\cdot HSCN$) [58] to SO_2 not only increased the arcing yield of the metallic sulfide fullerenes, a new isomer of the most abundant member of the family was observed, $Sc_2S@C_{3(6)}-C_{82}$ [66], along with the previously reported $Sc_2S@C_{3v(8)}-C_{82}$ (Fig. 3) [58,67].

A remarkable example of the complementarity of the shape and size of the encapsulated cluster and the carbon cage was reported

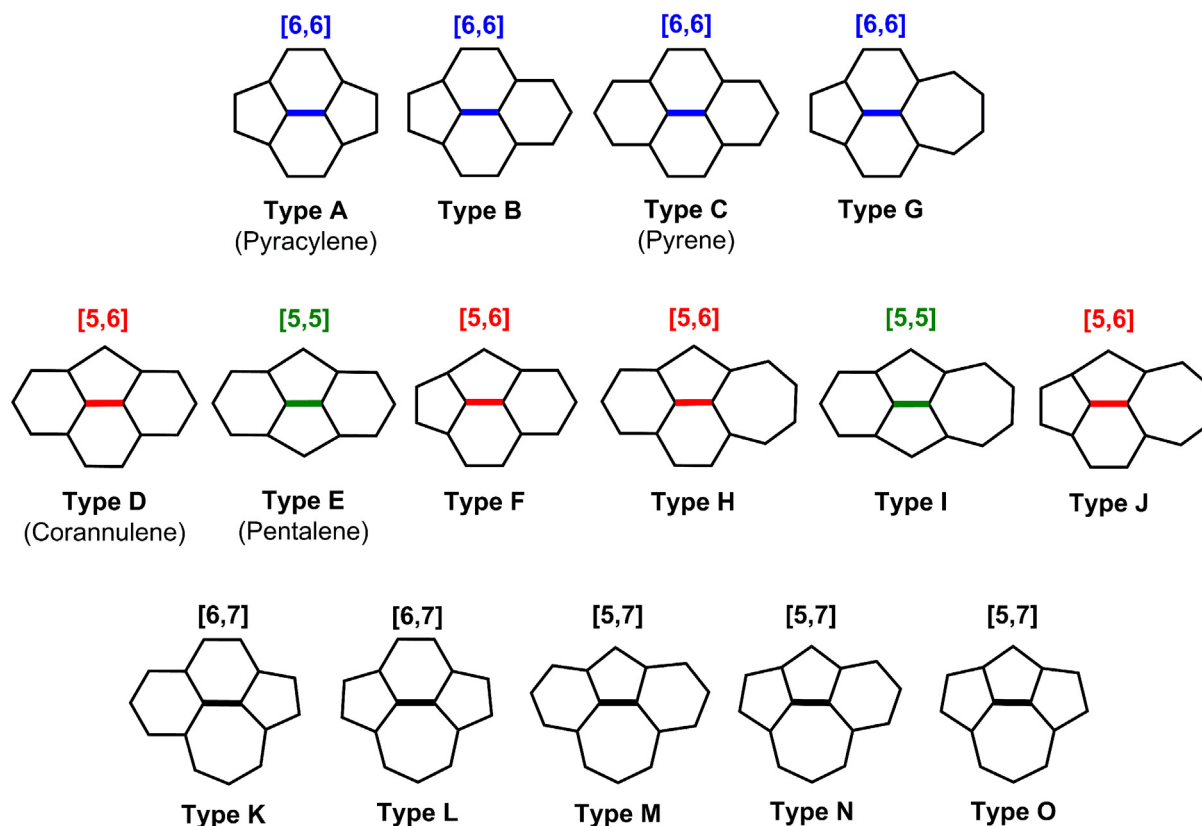


Fig. 1. Different types of possible C–C bonds in endohedral fullerenes. Types J and O proposed by DFT calculations [55].

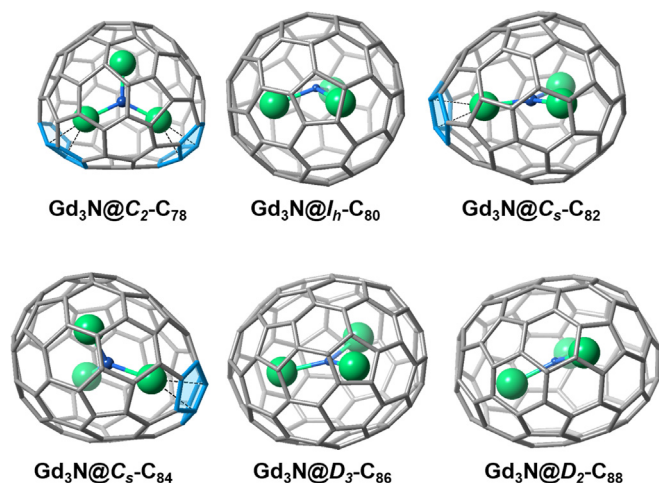


Fig. 2. Gadolinium nitride endohedral fullerene family ($\text{Gd}_3\text{N}@C_{2n}$, $n = 39\text{--}43$) [26,45,60–62,64,65].

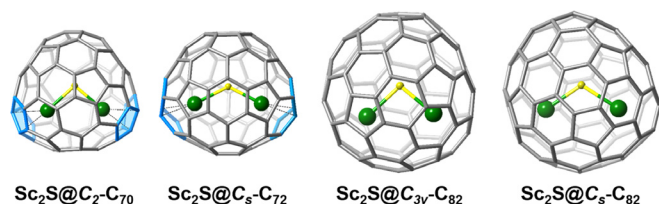


Fig. 3. Scandium sulfide endohedral fullerene family ($\text{Sc}_2\text{S}@C_{2n}$, $n = 35\text{--}50$) [66,72,73].

for two members of the dimetallic sulfide family. The IPR C_{72} carbon cage is the only empty fullerene which has never been isolated, while the IPR C_{70} carbon cage is the second most abundant fullerene. Thus while these are very different empty fullerenes, as EFs a close structural resemblance was observed, with the same encapsulated cluster, the same number of pentalene units and the same four-electron charge transfer from the cluster to the cage. In the case of $\text{Sc}_2\text{S}@C_{72}$, the chosen cage was $C_5(10,528)\text{-}C_{72}$, out of 11,189 possible non-IPR C_{72} isomers (Fig. 3). This cage is different from the three previously reported C_{72} endohedral isomers [68–71], highlighting the importance of the shape, size and charge complementarity of the encapsulated Sc_2S and the matching cage [72]. For $\text{Sc}_2\text{S}@C_{70}$, the $C_2(7892)\text{-}C_{70}$ cage was unambiguously assigned by experimental and computational studies out of 8149 possible C_{70} cages (Fig. 3). Interestingly, a single C_2 addition to a hexagon of $C_2(7892)\text{-}C_{70}$ gives rise to $C_5(10,528)\text{-}C_{72}$ without further rearrangements [73].

There are very few reports of EFs containing only transition metals trapped such as $\text{Ti}_2\text{C}_2@D_{3h}\text{-}C_{78}$ and $\text{Ti}_2@C_{84}$ [74–77]. In 2009, Yang and coworkers failed to synthesize titanium nitride EFs using pure TiO_2 , but when they used a $\text{TiO}_2\text{-Sc}_2\text{O}_3$ mixture they obtained the first mixed metallic titanium nitride EF, $\text{TiSc}_2\text{N}@I_h\text{-}C_{80}$. These results suggested that the only method to synthesize EFs containing titanium was by simultaneously using a rare metal [78]. In 2013, Echegoyen *et al.* changed the gas source from N_2 to SO_2 and used graphite rods packed with pure TiO_2 and graphite powder to successfully synthesize the first sulfide EF with no-rare metals inside, $\text{Ti}_2\text{S}@C_{78}$ [79]. Comparison of the UV–Vis absorption spectra of $\text{Ti}_2\text{S}@C_{78}$ with previously reported C_{78} isomers led to the assignment of the cage symmetry to the IPR $D_{3h}(24,109)\text{-}C_{78}$, confirmed by theoretical calculations. DFT calculations concluded that a six electron charge transfer occurs from the Ti_2S cluster to the C_{78} cage, and the encapsulated cluster is essentially linear (Ti-S-Ti 172° angle) [79].

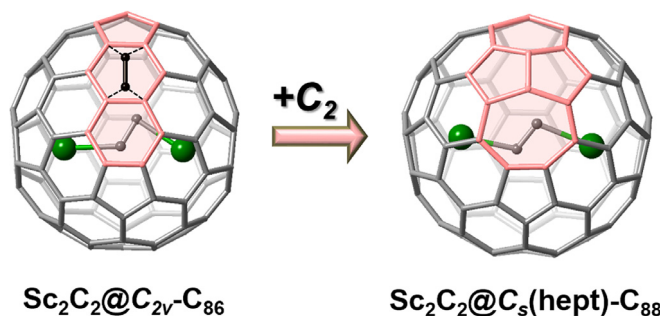


Fig. 4. Scandium carbide endohedral fullerenes; structural relationship between $\text{Sc}_2\text{C}_2@C_{2v}(9)\text{-}C_{86}$ and $\text{Sc}_2\text{C}_2@C_s(\text{hept})\text{-}C_{88}$ [84,85].

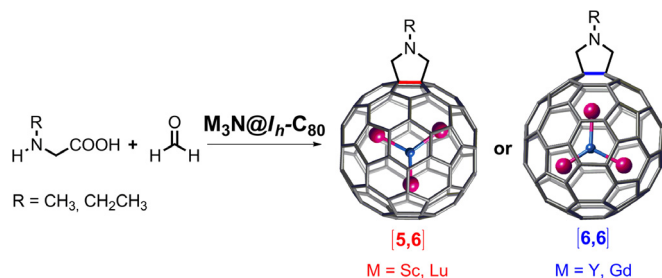
EFs with M_2C_{2n} composition are a challenge to unambiguously assign because they can exist as conventional EFs, $\text{M}_2@C_{2n}$, or as metal carbide EFs, $\text{M}_2\text{C}_2@C_{2n-2}$ [80]. Single crystal X-ray diffraction or DFT calculations are necessary to assign the correct structure. All reported cases of metal carbide EFs exhibited the M_2C_2 cluster in a folded butterfly shape with considerable disorder. This suggests that the cluster shape is influenced by the cage size; thus for larger cages a more linear M_2C_2 unit should be expected [81–83]. Recently, Chen *et al.* confirmed the previous assumption by reporting the synthesis, electrochemical and X-ray characterization of a planar twisted Sc_2C_2 cluster encapsulated in an unprecedented $C_{2v}(9)\text{-}C_{86}$ carbon cage [84]. Unanticipated, the $\text{Sc}_2\text{C}_2@C_{2v}(9)\text{-}C_{86}$ showed remarkable crystalline order which was explained by its unsymmetric shape and its dipolar nature (Fig. 4) [84].

Curious about the shape that the Sc_2C_2 unit would adopt inside larger carbon cages, Chen and co-workers isolated and characterized the metal carbide EF, $\text{Sc}_2\text{C}_2@C_{88}$ [85]. Interestingly, X-ray diffraction revealed a zigzag Sc_2C_2 cluster encapsulated in a never reported $C_s\text{-}C_{88}$ cage. Moreover, the cage possesses a heptagon ring which results from a C_2 insertion on the described $\text{Sc}_2\text{C}_2@C_{2v}(9)\text{-}C_{86}$ (Fig. 4). DFT calculations suggested that the observed $\text{Sc}_2\text{C}_2@C_s(\text{hept})\text{-}C_{88}$ is not the thermodynamically favored structure, and corresponds to a kinetically trapped species derived from $\text{Sc}_2\text{C}_2@C_{2v}(9)\text{-}C_{86}$ (Fig. 4) [85], providing strong evidence for the bottom-up growth mechanism of EFs [86].

3. Functionalization of endohedral fullerenes

3.1. 1,3-Dipolar cycloaddition

Even though $\text{Sc}_3\text{N}@I_h\text{-}C_{80}$ is the most abundant EF, its functionalization was not explored until 2005 because of its extremely low reactivity [87,88]. Cardona *et al.* reported the first fulleropyrrolidine derivative of $\text{Sc}_3\text{N}@I_h\text{-}C_{80}$ by using a 25-fold excess of *N*-ethyl glycine and a 125-fold excess of paraformaldehyde to yield regioselectively a [5,6]-pyrrolidine derivative (Scheme 1) [87]. After finding the conditions to functionalize cluster EFs, Echegoyen and co-workers studied the reactivity differences of cluster EFs, and found them to be dictated by the encapsulated metal cluster [45,89–91]. Remarkably, when the same reaction conditions were applied for $\text{Y}_3\text{N}@I_h\text{-}C_{80}$ the [6,6]-pyrrolidine derivative was initially observed, but slowly isomerized to the thermodynamically preferred [5,6]-pyrrolidine isomer [45,89,90,92]. The influence of the size of the encapsulated cluster on the 1,3-dipolar cycloaddition of azomethine ylide to $\text{M}_3\text{N}@I_h\text{-}C_{80}$ was also explored by Cai *et al.* and Chen *et al.* who demonstrated that when the encapsulated clusters fit perfectly planar inside ($\text{M} = \text{Sc}$ and Lu) the [5,6]-mono-adduct is the thermodynamically preferred product [91], whereas for larger metals such as Y and Gd the encapsulated clus-



Scheme 1. 1,3-Dipolar cycloaddition of azomethine ylide on $\text{M}_3\text{N}@I_h\text{-C}_{80}$ ($\text{M} = \text{Sc, Lu, Y, Gd}$) [95].

ter is pyrimidalized and the [6,6]-*mono*-adduct is the preferred product (Scheme 1) [45,93,89,94].

It is well-known that fulleropyrrolidines undergo *retro*-cycloaddition reactions leading to the pristine fullerene and non-fullerene side products [96]. In 2006, Martin et al. used the same conditions previously reported [87], to perform the 1,3-dipolar cycloaddition reaction to a mixture of $\text{Sc}_3\text{N}@D_{3h}\text{-C}_{78}$ and the two isomers of $\text{Sc}_3\text{N}@C_{80}$, I_h and D_{5h} . Due to the higher reactivity of $\text{Sc}_3\text{N}@D_{3h}\text{-C}_{78}$ and $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$, they selectively isolated the [5,6]-*mono*-adduct of $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$ and multiadducts of the other two EFs, and the subsequent *retro*-cycloaddition of the *mono*-adduct yielded pure $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$ [96]. This strategy was also applied to obtain $\text{Y}_3\text{N}@I_h\text{-C}_{80}$ from its [5,6]-*mono*-adduct [96]. Electrochemical *retro*-cycloaddition was also explored for the *N*-ethyl pyrrolidine of C_{60} and $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$ by controlled-potential oxidative electrolysis leading to the pure pristine fullerenes in both cases [96,97].

3.2. Bingel-Hirsch cyclopropanation

In 2005, Cardona and coworkers reported the first Bingel-Hirsch addition to EFs. Addition-elimination of bromo diethylmalonate to $\text{Y}_3\text{N}@I_h\text{-C}_{80}$ in the presence of DBU and *o*-DCB selectively yielded the [6,6]-methano derivative, and similar results were obtained when using $\text{M}_3\text{N}@I_h\text{-C}_{80}$ ($\text{M} = \text{Gd}$ and Lu) [98,99]. However, when $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$ was used in place of $\text{Y}_3\text{N}@I_h\text{-C}_{80}$, no products were detected, emphasizing the drastic difference in reactivity of $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$ compared to its homologous endohedrals [100]. In 2010, Pinzón and coworkers modified the Bingel reaction conditions by adding DMF to the solvent mixture to successfully synthesize the first [6,6]-Bingel derivative of $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$. According to Pinzón et al., DMF stabilized the transition state ylide during the elimination step allowing the isolation of the [6,6]-*mono*-adduct [100].

In 2015, Solà and coworkers used DFT calculations to study the Bingel-Hirsch addition to the thirteen non-equivalent bonds of $\text{Sc}_3\text{N}@D_{3h}\text{-C}_{78}$ and proposed the predicted aromaticity criterion (PAC). This criterion helps to identify the most reactive bonds of any given EF solely based on a simple evaluation of the cage structure (Fig. 5) [101]. Echegoyen et al. verified the validity of PAC for $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$. Bingel-Hirsch cyclopropanation of $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$ yielded three *mono*-adduct isomers. The major *mono*-adduct isomer was assigned as an unsymmetric isomer by ^1H NMR as predicted by the PAC and the addition likely occurred at bond 3 (Fig. 5), while the other two isomers were assigned as unsymmetric and symmetric isomers by ^1H NMR, in agreement with the PAC predictions, additions at bonds 1 and 2 respectively [101].

Chaur et al. studied the cage size effect for the Bingel-Hirsch reaction on four members of the $\text{Gd}_3\text{N}@C_{2n}$ ($n = 40, 41, 42, 44$) family. When standard conditions were used with $\text{Gd}_3\text{N}@I_h\text{-C}_{80}$, both [6,6]-*mono*-adduct and *bis*-adducts were observed instantaneously.

Int 1 Identify the least aromatic positions:

↓ C-666 > C-566

Int 2 Count the number of 5MR in the α positions:

↓ 3 > 2 > 1 > 0

TS 1 Ring closure: the best nucleophile.

↓ 5-MR > 6-MR

TS 2 Less aromatic ring, lowest TS.

↓ 5-MR(Y) - 3 > 5-MR(Z) - 4

Kinetic Bingel Derivative

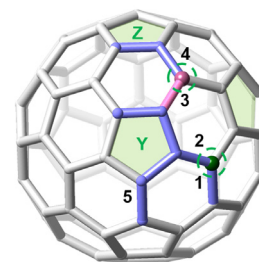


Fig. 5. Predicted aromaticity criteria (PAC) for Bingel-Hirsch cycloadditions.

On the other hand, when $\text{Gd}_3\text{N}@C_{82}$ and $\text{Gd}_3\text{N}@C_{84}$ were used *mono*-adducts were detected only after 20 min of reaction and no further additions were observed. For the largest member of the family, $\text{Gd}_3\text{N}@D_{2-C_{88}}$ no cyclopropanated products were obtained. These results indicated that the reactivity increases as the cage size decreases, thus for smaller cages a higher degree of pyramidalization at the C atoms and cage strain results in an increase in the reactivity [99,102].

3.3. Electrosynthesis and [3+2] cycloaddition

Electrochemical synthesis methods using EFs involve anionic fullerene species generated by electrochemical reduction to produce methano derivatives regioselectively [95,103]. These derivatives are not accessible by typical synthetic procedures. Li et al. reported the reactivity differences of anionic EFs depend on the nature of the encapsulated cluster. Under identical conditions, $[\text{Sc}_3\text{N}@I_h\text{-C}_{80}]^{2-}$ was completely unreactive with benzal bromide (PhCHBr_2) while $[\text{Lu}_3\text{N}@I_h\text{-C}_{80}]^{2-}$ yielded the [6,6]-methano derivative $\text{Lu}_3\text{N}@I_h\text{-C}_{80}(\text{CHC}_6\text{H}_5)$ [104]. DFT calculations were used to rationalize these reactivity differences by showing that $[\text{Sc}_3\text{N}@I_h\text{-C}_{80}]^{2-}$ exhibits low nucleophilicity because its charge density is mainly localized on the encapsulated cluster and not on the cage. The corresponding trianion $[\text{Sc}_3\text{N}@I_h\text{-C}_{80}]^{3-}$ has higher charge density localized on the cage and was consequently able to react with benzal bromide to selectively produce the [6,6]-methano derivative $\text{Sc}_3\text{N}@I_h\text{-C}_{80}(\text{CHC}_6\text{H}_5)$ [105].

There is only one example of an EF derivative in an organic photovoltaic (OPV) solar cell: $\text{PCBH-Lu}_3\text{N}@I_h\text{-C}_{80}$, which yielded a power conversion efficiency (PCE) of 4.2% [106]. For this reason, we recently functionalized EFs with two addends, the diphenylamine (DPM) addend and the PCBM addend, since the corresponding empty fullerene derivatives performed very well in OPV [107–111]. Functionalization of the least reactive EF $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$ using the DPM addend resulted in the synthesis of the first [5,6]-methano adduct [112]. The reaction exhibited high yield under relative mild conditions which is unusual for EFs [102,113,114]. The [6,6]-methano adduct showed very similar redox properties to those of $\text{PCBH-Lu}_3\text{N}@I_h\text{-C}_{80}$, suggesting that this compound could potentially be an effective acceptor in OPV devices [112].

Functionalization of a $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$ and $\text{Sc}_3\text{N}@D_{3-C_{68}}$ mixture using the PCBM addend led to the isolation of pure $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$ and derivatized $\text{Sc}_3\text{N}@D_{3-C_{68}}$ [48]. Highly regioselective formation of two out of thirty-four possible regioisomers was observed for $\text{Sc}_3\text{N}@D_{3-C_{68}}$, possibly directed by the encapsulated cluster and the presence of the three pentalene units. PCBM functionalization of $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$ gave rise to five out of fifteen possible regioisomers, while $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$ yielded only one isomer [115]. The increase in the number of isomers observed was explained by the lower symmetry of $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$ compared to the highly symmetric $I_h\text{-C}_{80}$ isomer and to the free rotation of the encapsulated cluster of $D_{5h}\text{-C}_{80}$ compared to the rotationally locked cluster in $\text{Sc}_3\text{N}@D_{3-C_{68}}$ [48].

4. Bis-1,3-dipolar cycloaddition of $M_3N@I_h-C_{80}$ ($M = Lu, Y$ and Er)

To date, the derivatization of trimetallic nitride EFs has been focused primarily on the isolation and characterization of *mono*-addition products [95,103,116], but a few derivatizations have reported the regiochemistry and properties of some *bis*-addition products [14,117,118]. Recently, it has been shown that some regioisomerically pure empty fullerene *bis*-adducts perform better in OPV solar cells than their corresponding isomeric mixtures [119,120]. Consequently, we investigated the controlled multifunctionalization of $M_3N@I_h-C_{80}$ ($M = Sc$ and Lu) using two different methods: the tether-controlled *bis*-addition reaction [121–123] and the independent (non-tethered) *bis*-1,3-dipolar cycloaddition [117]. Surprisingly, using the tether method no detectable amounts of *bis*-derivatives were observed, while the independent cycloadditions yielded a very limited number of *bis*-adducts, three for $Sc_3N@I_h-C_{80}$ and two for $Lu_3N@I_h-C_{80}$ out of the 91 statistically possible regioisomers [117]. Taking into account the large number of statistically possible *bis*-adduct isomers on an I_h-C_{80} cage and the strong influence of the size of the encapsulated cluster [117], we did a comprehensive study of *bis*-additions using different cluster endohedral fullerenes, including $M_3N@I_h-C_{80}$ ($M = Lu, Y$ and Er). Although *bis*-1,3-dipolar cycloadditions to $M_3N@I_h-C_{80}$ ($M = Lu$ and Y) have been reported [117,118], some minor isomers observed were not characterized. Here we report for the first time the synthesis and characterization of two minor *bis*-adduct isomers of $M_3N@I_h-C_{80}$ ($M = Lu$ and Y) and three additional *bis*-adduct isomers of $Er_3N@I_h-C_{80}$.

4.1. $M_3N@I_h-C_{80}$ ($M = Lu, Y$ and Er) Bisadducts characterization

Bis-adducts **1–4** were synthesized using $Lu_3N@I_h-C_{80}$ and purified by silica gel column chromatography and preparative TLC following previously reported procedures [117]. Characterization of isomers **1** and **2** was reported elsewhere [117], while isomers **3** and **4** are reported here for the first time (Scheme 2). The matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra of *bis*-adducts **3** and **4** showed molecu-

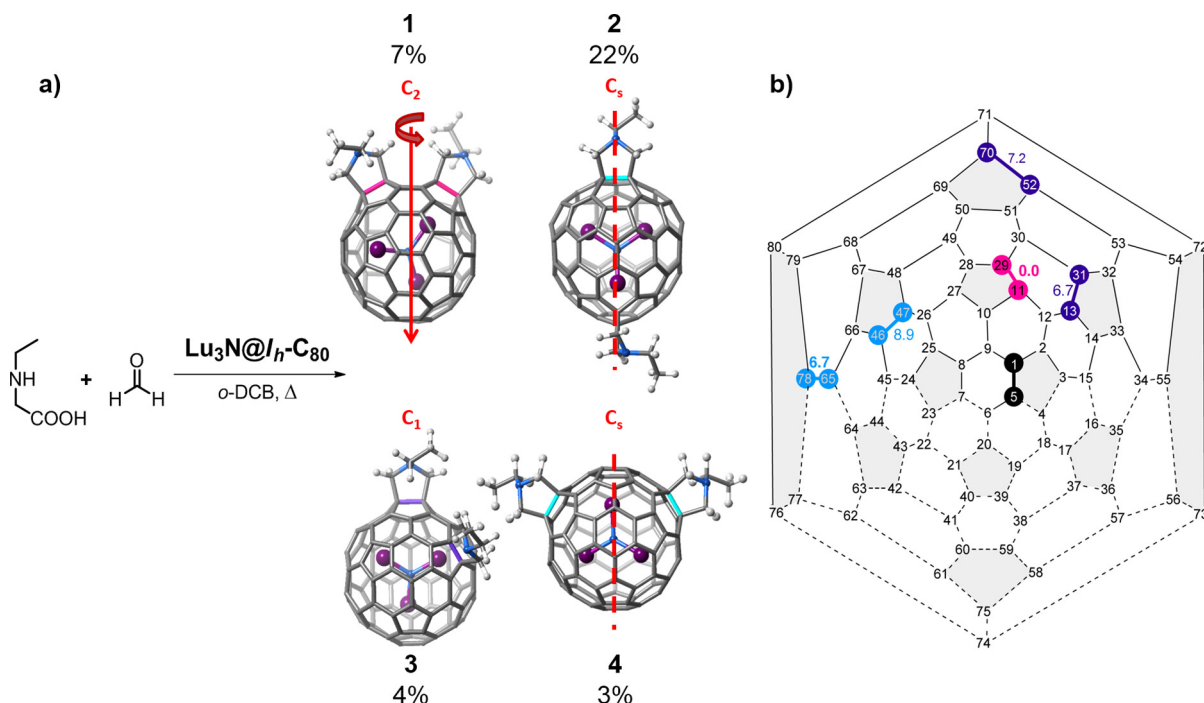
lar peaks at 1252.0095 and 1252.0278 m/z respectively, corresponding to *bis*-adduct regio-isomers.

The 1H NMR spectrum of *bis*-adduct **3** exhibited four AB quartets corresponding to the unequivalent protons of the pyrrolidine rings and one multiplet for the methylenes of the *N*-ethyl groups (Fig. 6). Therefore, *bis*-adduct **3** is an unsymmetric regio-isomer, similar to the one reported for $M_3N@C_{80}$ ($M = Sc$ and Y) [117,118]. Due to the lack of symmetry of *bis*-adduct **3** and the large number of possible C_1 -symmetric regioisomers (sixty-three), based solely on NMR we cannot assign it to a specific isomer. As a result of the similar stability of [5,6]- and [6,6]-*mono*-adducts for $Lu_3N@I_h-C_{80}$, we considered all 63 possible C_1 -symmetric *bis*-adduct regioisomers and used the energy values of the optimized geometries previously reported by density functional theory (DFT) [117]. DFT calculations indicated that the preferred unsymmetrical *bis*-addition site for $Lu_3N@I_h-C_{80}$ corresponds to the bond denoted as 31–13 or 52–70 (see Scheme 2b for bond assignments and relative stabilities).

The 1H NMR spectrum of *bis*-adduct **4** shows a more symmetric resonance pattern, with two AB quartets corresponding to the methylenes of the pyrrolidines and one quartet corresponding to the methylenes of the *N*-ethyl groups (Fig. 6). This must be one of the 18 possible C_s -symmetric regioisomers. DFT calculations of all 18 possible C_s -symmetric regioisomers indicated that the preferred second addition site is bond 46–47, which corresponds to the same C_s -symmetric *bis*-adduct regioisomer reported for $Sc_3N@I_h-C_{80}$ (Scheme 2b) [117].

The redox potentials of $Lu_3N@I_h-C_{80}$ *bis*-adduct regioisomers were measured by cyclic voltammetry in *o*-DCB solutions (Figs. S5 and S9). The CV of **3** and **4** exhibited irreversible reduction processes analogous to those observed for $Lu_3N@I_h-C_{80}$ and *bis*-adducts **1** and **2** [103,117,124]. In contrast to $Lu_3N@I_h-C_{80}$, *bis*-adducts **3** and **4** showed irreversible oxidation processes cathodically shifted approximately 430 mV and 580 mV, respectively, similar to *bis*-adducts **1** and **2** [117].

Yamakoshi *et al.* previously assigned the main *bis*-adduct **5** regioisomer of $M_3N@I_h-C_{80}$ ($M = Y$ and Gd) based on NMR spectroscopic and DFT calculations as one of the 18 possible



Scheme 2. a) Bisadduct regioisomers obtained from the *bis*-1,3-dipolar cycloaddition on $Lu_3N@I_h-C_{80}$. b) Schlegel representation of observed [5,6]-[5,6]- and [5,6]-[6,6]-*bis*-adducts and their DFT relative stabilities (in kcal/mol). The first adduct is always attached to bond 1–5 [117].

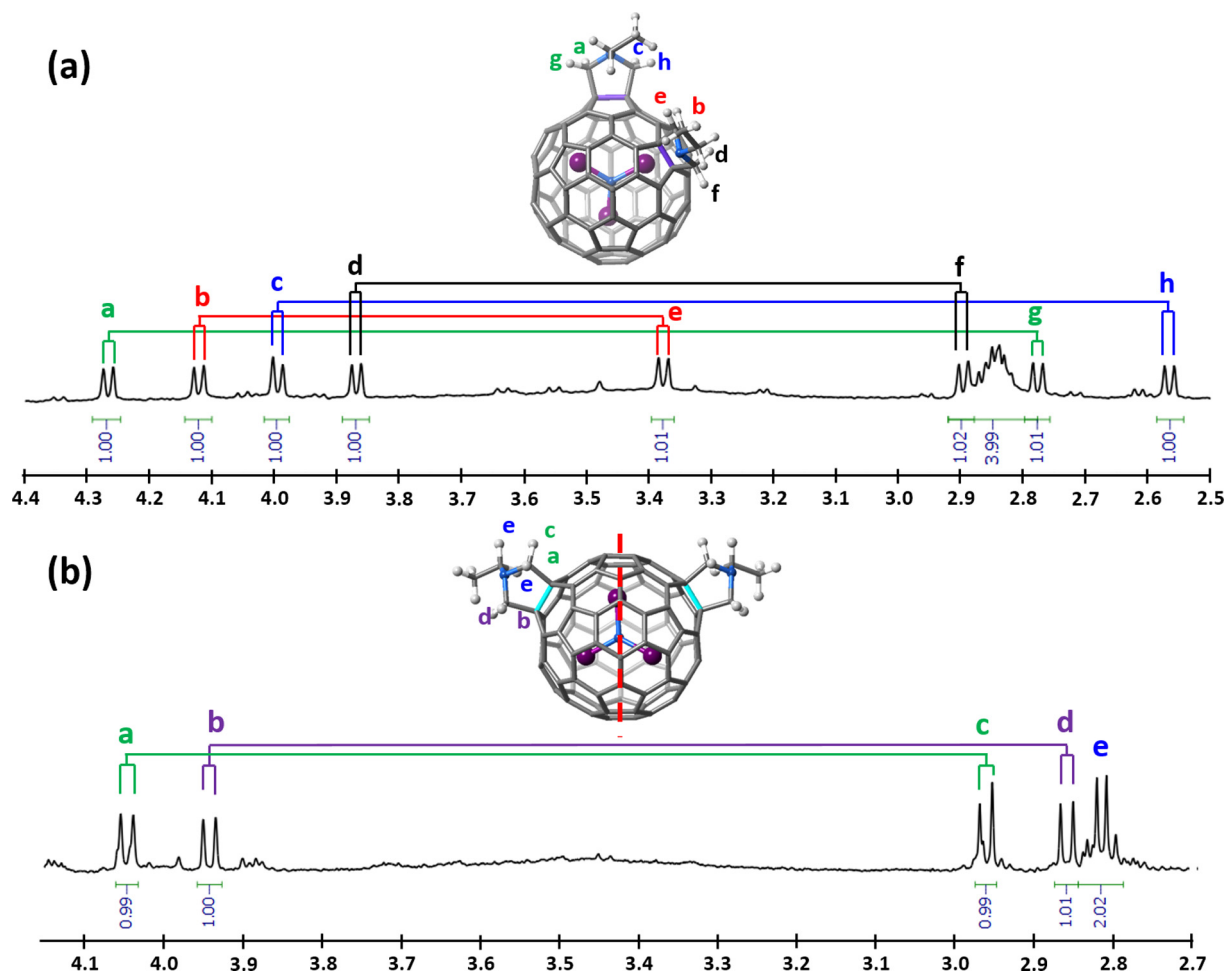
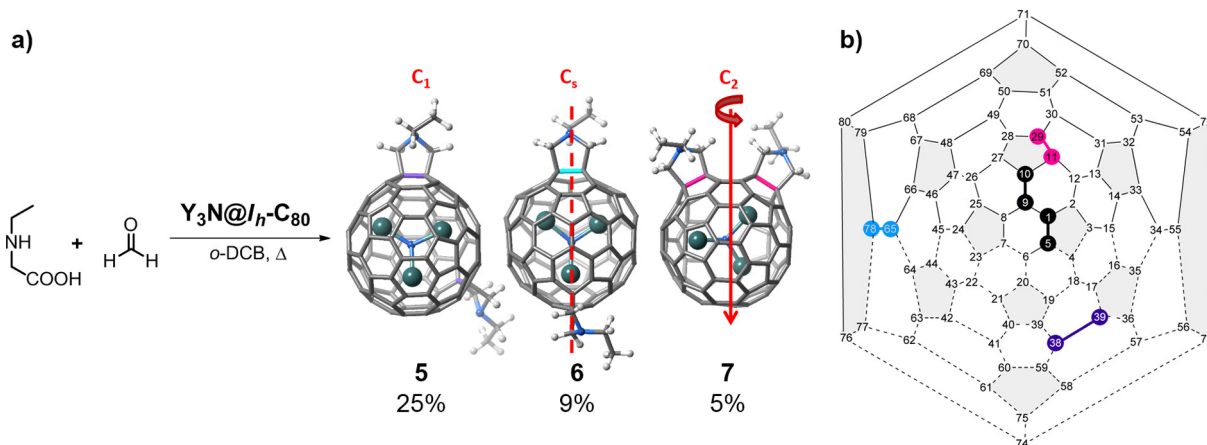


Fig. 6. ^1H NMR spectrum of (a) *bis*-adduct **3**, (b) *bis*-adduct **4** (600 MHz; $\text{CDCl}_3/\text{CS}_2$ 1:1, 298 K); assignments based on the observed spectral symmetry, the ^1H – ^1H COSY NMR spectra and DFT calculations [117].

[6,6]-[6,6]-unsymmetric *bis*-adducts [118]. Here we report two minor *bis*-adduct regioisomers **6** and **7** (Scheme 3). *Bis*-adducts **5**–**7** were synthesized using $\text{Y}_3\text{N}@I_h\text{-C}_{80}$ and purified by silica gel column chromatography and preparative TLC following the previously reported procedure [117,118]. The matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra of **6** and **7** showed molecular peaks at 1383.9965 and 1383.9475 m/z respectively, corresponding to *bis*-adduct regio-isomers.

The ^1H NMR spectrum of **6** shows a high degree of symmetry, similar to the one reported for $\text{Lu}_3\text{N}@C_{80}$ [117], with two uncorrelated singlets at 4.60 and 4.40 ppm (from COSY and NOESY spectra) corresponding to a [6,6]-pyrrolidine and one AB quartet at 4.48 and 3.10 ppm. Thus, the [5,6]-pyrrolidine must be perpendicular to the [6,6]-pyrrolidine so that neither adduct breaks the symmetry of the other. We also observed two symmetrically inequivalent quartets for the methylenes of the *N*-ethyl groups at



Scheme 3. a) Bisadduct regioisomers obtained from the *bis*-1,3-dipolar cycloaddition on $\text{Y}_3\text{N}@I_h\text{-C}_{80}$. b) Schlegel representation of observed [5,6]-[5,6]-, [5,6]-[6,6]- and [6,6]-[6,6]-*bis*-adducts. The first adduct for **5** is attached to bond 9–10, while for **6** and **7** to bond 1–5 [118].

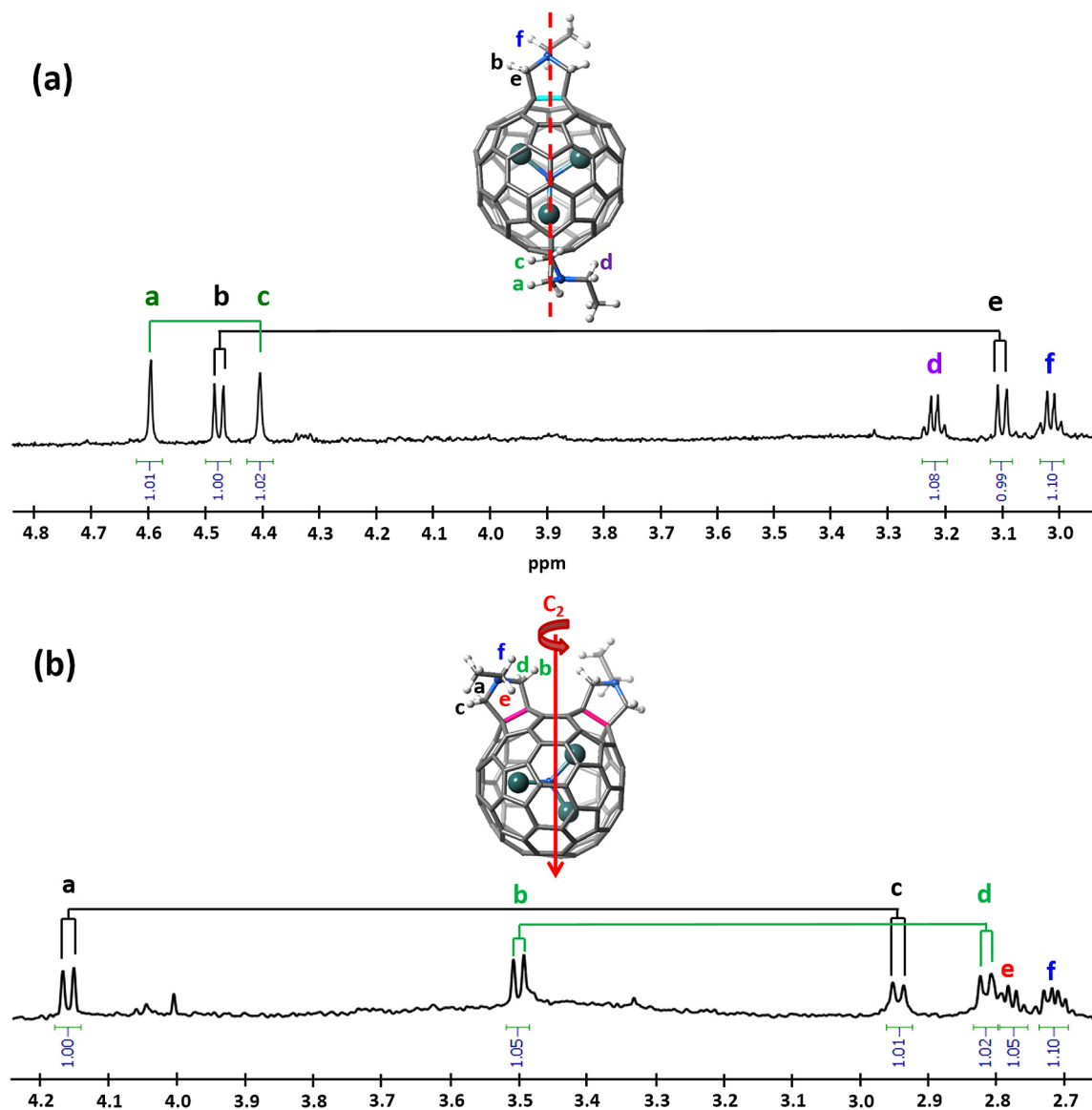


Fig. 7. ^1H NMR spectrum of (a) *bis*-adduct **6**, (b) *bis*-adduct **7** (600 MHz; $\text{CDCl}_3/\text{CS}_2$ 1:1, 298 K); assignments based on the observed spectral symmetry, the ^1H – ^1H COSY NMR spectra and DFT calculations [117].

3.22 and 3.01 ppm for the [5,6]- and [6,6]-pyrrolidines, respectively (Fig. 7). Interestingly, the UV–Vis spectrum of this mixed (hybrid) **6** is essentially identical as the one reported for $\text{Lu}_3\text{N}@I_h\text{-C}_{80}$ **2** (Fig. S12) indicating that the second addition likely occurred at bond 65–78 (Scheme 3b) [117].

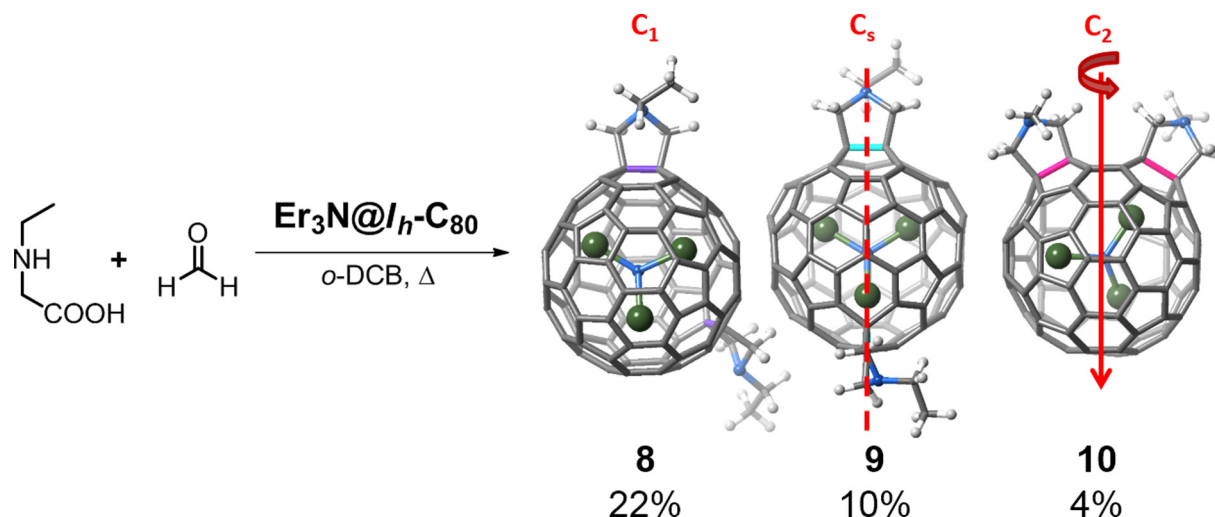
The ^1H NMR spectrum of *bis*-adduct **7** exhibited a very similar resonance pattern to that of $\text{Lu}_3\text{N}@I_h\text{-C}_{80}$ *bis*-adduct **1** [117], with two AB quartets corresponding to the methylenes of the pyrrolidines and an ABX₃ system corresponding to the methylenes of the *N*-ethyl groups. Therefore, this regioisomer corresponds to one of the 5 C_2 -symmetric chiral [5,6]-[5,6]-*bis*-adducts (Fig. 7). Remarkably, the UV–Vis spectrum of this chiral *bis*-adduct **7** is essentially identical to the one reported for $\text{Lu}_3\text{N}@I_h\text{-C}_{80}$ derivative **1** (Fig. S16), thus the second addition site for **7** is likely on bond 11–29 (Scheme 3b) [117].

The redox potentials of the two minor *bis*-adduct regioisomers of $\text{Y}_3\text{N}@I_h\text{-C}_{80}$ were measured by cyclic voltammetry in *o*-DCB solutions (Figs. S14 and S18). The CV of **6** and **7** exhibited irreversible reduction processes analogous to those observed for the pristine fullerene $\text{Y}_3\text{N}@I_h\text{-C}_{80}$ [103,124]. **6** and **7** showed irreversible oxidation processes cathodically shifted compared to that

of $\text{Y}_3\text{N}@I_h\text{-C}_{80}$ by approximately 360 mV and 150 mV respectively, so these should act as better donors.

Bis-1,3-dipolar cycloadditions to $\text{Er}_3\text{N}@I_h\text{-C}_{80}$ resulted in the isolation of three *bis*-adducts, but due to the paramagnetic nature of erbium, we were not able to characterize the *bis*-adduct regioisomers by NMR spectroscopy. However, we were able to assign the addition patterns and symmetry of the regioisomers solely based on the unique UV–Vis absorption pattern of the three $\text{Er}_3\text{N}@I_h\text{-C}_{80}$ *bis*-adducts and the previously mentioned $\text{M}_3\text{N}@I_h\text{-C}_{80}$ ($\text{M} = \text{Lu}$ and Y) regioisomers (Scheme 4, Figs. S22, S24, S27). Hence, the main *bis*-adduct **8** corresponds to the [6,6]-[6,6]-unsymmetric regioisomer with the second addition site on bond 38–39 (Scheme 3b), the second isomer **9** to the hybrid [5,6]-[6,6] C_s -symmetric regioisomer with the second addition site on bond 65–78 (Scheme 3b) and the third isomer **10** to the chiral [5,6]-[5,6] C_2 -symmetric regioisomer with the second addition site on bond 11–29 (Scheme 3b) [117].

The redox potentials of *bis*-adduct **9** of $\text{Er}_3\text{N}@I_h\text{-C}_{80}$ were measured by cyclic voltammetry in *o*-DCB solutions (Fig. S25). The CV of **9** exhibited irreversible reduction processes analogous to those observed for the pristine fullerene $\text{Er}_3\text{N}@I_h\text{-C}_{80}$ [124]. **9** also



Scheme 4. Bis-adduct regioisomers obtained from the bis-1,3-dipolar cycloaddition on $\text{Er}_3\text{N@I}_h\text{-C}_{80}$.

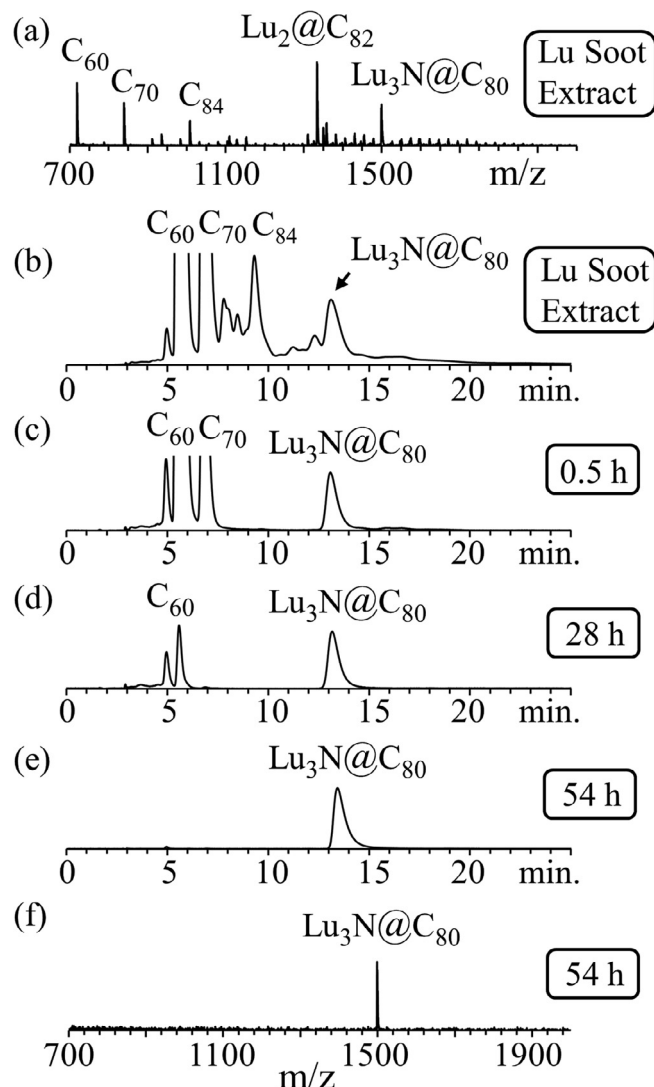


Fig. 8. (a) LDI mass spectrum and (b) HPLC analysis of Lu soot extract, and fullerenes remaining in solution after (c) 0.5 h (d) 28 h, and (e, f) 54 h, to obtain purified $\text{Lu}_3\text{N@I}_h\text{-C}_{80}$. HPLC conditions: BuckyPrep-M column, 1 mL/min xylenes, 360 nm UV detection and 200 μL injection.

showed irreversible oxidation processes cathodically shifted compared to that of $\text{Er}_3\text{N@I}_h\text{-C}_{80}$ by approximately 400 mV, similar to all previously mentioned bis-adduct regioisomers.

4.2. Purification of $\text{Lu}_3\text{N@I}_h\text{-C}_{80}$ and $\text{Er}_3\text{N@I}_h\text{-C}_{80}$ using chemical methods

In contrast to empty-cage fullerenes, electron-rich $\text{M}_3\text{N@I}_h\text{-C}_{80}$ EF cages ($\text{M} = \text{Sc}, \text{Y}, \text{Lu}, \text{Er}, \text{Tb}, \text{Ho}, \text{and Gd}$) possess a lower reactivity to amines. This reactivity difference permits a chemical-based separation method that immobilizes fullerene contaminants onto aminosilica [125]. In the Stir and Filter Approach (SAFA), the addition of diaminosilica to solutions of soot extract yields isomerically pure $\text{Sc}_3\text{N@I}_h\text{-C}_{80}$ [125,126]. While investigating the deleterious effect of “wet” solvents and “wet” aminosilica on the SAFA technique, $\text{Er}_3\text{N@I}_h\text{-C}_{80}$ was also purified [127]. Detailed in the [supplemental material](#), the $\text{Er}_3\text{N@I}_h\text{-C}_{80}$ sample used in this bis-adduct study was isolated in a similar manner.

However, the SAFA isolation of $\text{Lu}_3\text{N@I}_h\text{-C}_{80}$ is new, and details are now described. To ensure sufficient amounts of purified $\text{Lu}_3\text{N@I}_h\text{-C}_{80}$ sample for bisadduct experiments, 2.2 g of Lu soot extract (Fig. 8a, b) was dissolved in 1.5 L of freshly opened anhydrous xylenes. To this stirring solution was added 300 g of synthesized diaminosilica [125], which was vacuum dried overnight at 60 °C and immediately used after backfilling the oven with Ar and cooling under inert gas. To monitor the uptake and immobilization of fullerene contaminants, aliquots were taken at arbitrary times of 0.5 h (Fig. 8c) and 28 h (Fig. 8d). After 54 h of reaction, the reaction slurry was filtered, and the filtrate (Fig. 8e, f) contained isomerically pure $\text{Lu}_3\text{N@I}_h\text{-C}_{80}$. Upon solvent removal and subsequent ether washing, 25 mg of purified $\text{Lu}_3\text{N@I}_h\text{-C}_{80}$ was obtained.

5. Conclusion

There are still many challenges to overcome in the synthesis of new EFs in order to improve their yields and separation. Functionalization of endohedral fullerenes has helped to increase their solubilities and potential applications, but many new derivatives and EFs remain to be prepared and characterized.

New bis-adducts of endohedral metallofullerenes $\text{Lu}_3\text{N@I}_h\text{-C}_{80}$, $\text{Y}_3\text{N@I}_h\text{-C}_{80}$ and $\text{Er}_3\text{N@I}_h\text{-C}_{80}$ have been isolated via bis-1,3-cycloaddition reaction and characterized using mass spectrometry, UV–Vis, NMR spectroscopy and electrochemistry. The remarkable regioselectivity is attributed to the strong influence of the internal

trimetallic nitride cluster. Out of 91 possible *bis*-adduct isomers, we obtained four *bis*-adducts for $\text{Lu}_3\text{N}@I_h\text{-C}_{80}$ and three *bis*-adducts for $\text{M}_3\text{N}@I_h\text{-C}_{80}$ ($\text{M} = \text{Y}$ and Er). Though the factors controlling the regiochemistry of multiple additions to EFs are still uncertain, these findings provide new insight and rationale for the synthesis and study of multiadducts of endohedral metallofullerenes. We also observed that each *bis*-adduct regio-isomer of $\text{M}_3\text{N}@I_h\text{-C}_{80}$ showed a unique UV–Vis absorption pattern independent of the encapsulated metal, which should help to identify new *bis*-adducts by simple comparison of their UV–Vis absorption spectra. Two *bis*-adduct regioisomers, [5,6]-[5,6]-chiral and [5,6]-[6,6]-hybrid, were detected for different metal nitride encapsulated clusters $\text{M}_3\text{N}@I_h\text{-C}_{80}$ ($\text{M} = \text{Lu}, \text{Y}, \text{Er}$).

Acknowledgments

This work was supported by the National Science Foundation [grant number CHE-1408865]; the PREM Program [grant number DMR-1205302]; the Robert A. Welch Foundation [grant number AH-0033]; SS thanks the NSF for financial support from RUI [grant number CHE-1465173].

Appendix A. Supplementary data

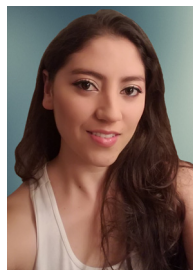
Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.ica.2017.03.040>.

References

- [1] H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, R.E. Smalley, C_{60} : buckminsterfullerene, *Nature* 318 (1985) 162–163.
- [2] W. Kratschmer, L.D. Lamb, K. Fostiropoulos, D.R. Huffman, Solid C_{60} : a new form of carbon, *Nature* 347 (1990) 354–358.
- [3] Q. Xie, E. Perez-Cordero, L. Echegoyen, Electrochemical detection of C_{60} - and C_{70} - enhanced stability of fullerenes in solution, *J. Am. Chem. Soc.* 114 (1992) 3978–3980.
- [4] Q. Xie, F. Arias, L. Echegoyen, Electrochemically-reversible, single-electron oxidation of C_{60} and C_{70} , *J. Am. Chem. Soc.* 115 (1993) 9818–9819.
- [5] Y. Yang, F. Arias, L. Echegoyen, L.P.F. Chibante, S. Flanagan, A. Robertson, L.J. Wilson, Reversible fullerene electrochemistry: correlation with the HOMO–LUMO energy difference for C_{60} , C_{70} , C_{76} , C_{78} , and C_{84} , *J. Am. Chem. Soc.* 117 (1995) 7801–7804.
- [6] C. Boudon, J.-P. Gisselbrecht, M. Gross, A. Herrmann, M. Ruettimann, J. Crassous, F. Cardullo, L. Echegoyen, F. Diederich, Redox characteristics of covalent derivatives of the higher fullerenes C_{70} , C_{76} , and C_{78} , *J. Am. Chem. Soc.* 120 (1998) 7860–7868.
- [7] F. Arias, Q. Xie, L. Echegoyen, Y. Wu, Q. Lu, S.R. Wilson, Kinetic effects in the electrochemistry of fullerene derivatives at very negative potentials, *J. Am. Chem. Soc.* 116 (1994) 6388–6394.
- [8] F. Arias, L. Echegoyen, S.R. Wilson, Q. Lu, Q. Lu, Methanofullerenes and methanofulleroids have different electrochemical behavior at negative potentials, *J. Am. Chem. Soc.* 117 (1995) 1422–1427.
- [9] R. Kessinger, M. Gomez-Lopez, C. Boudon, J.-P. Gisselbrecht, M. Gross, L. Echegoyen, F. Diederich, Walk on the sphere: electrochemically induced isomerization of C_{60} *bis*-adducts by migration of di(alkoxycarbonyl)methano bridges, *J. Am. Chem. Soc.* 120 (1998) 8545–8546.
- [10] J.-P. Bourgeois, L. Echegoyen, M. Fabbrioli, E. Pretsch, F. Diederich, Regioselective synthesis of trans-1 fullerene *bis*-adducts directed by a crown ether tether: alkali metal cation modulated redox properties of fullerene-crown ether conjugates, *Angew. Chem. Int. Ed.* 37 (1998) 2118–2121.
- [11] L. Echegoyen, L.E. Echegoyen, Electrochemistry of fullerenes and their derivatives, *Acc. Chem. Res.* 31 (1998) 593–601.
- [12] M.J. van Eis, P. Seiler, F. Diederich, R.J. Alvarado, L. Echegoyen, First tether-directed regioselective *bis*-functionalization of C_{70} : effects of cation complexation on the redox properties of diastereoisomeric fullerene crown ether conjugates, *Chem. Commun. (Cambridge)* (2000) 1859–1860.
- [13] M.J. van Eis, P. Seiler, L.A. Muslinkina, M. Badertscher, E. Pretsch, F. Diederich, R.J. Alvarado, L. Echegoyen, I.P. Nunez, Supramolecular fullerene chemistry: a comprehensive study of cyclophane-type mono- and *bis*-crown ether conjugates of C_{70} , *Helv. Chim. Acta* 85 (2002) 2009–2055.
- [14] M.R. Cerón, L. Echegoyen, Recent progress in the synthesis of regio-isomerically pure *bis*-adducts of empty and endohedral fullerenes, *J. Phys. Org. Chem.* 29 (2016) 613–619.
- [15] P.L. Boulas, Y. Zuo, L. Echegoyen, A new route for the selective synthesis of [6,6]-methanofullerenes. Electrosynthesis of $\text{C}_{61}\text{HfMe}_3$ and C_{61}HfCN , *Chem. Commun.* (1996) 1547–1548.
- [16] J. Crassous, J. Rivera, N.S. Fender, L. Shu, L. Echegoyen, C. Thilgen, A. Herrmann, F. Diederich, Chemistry of C_{84} : separation of three constitutional isomers and optical resolution of $\text{D}_{2d}\text{-C}_{84}$ by using the “bingel–retro-bingel” strategy, *Angew. Chem. Int. Ed.* 38 (1999) 1613–1617.
- [17] N.N.P. Moonen, C. Thilgen, L. Echegoyen, F. Diederich, The chemical retro-Bingel reaction: selective removal of bis(alkoxycarbonyl)methano addends from C_{60} and C_{70} with amalgamated magnesium, *Chem. Commun.* 335–336 (2000).
- [18] M.W.J. Beulen, L. Echegoyen, J.A. Rivera, M.A. Herranz, A. Martin-Domech, N. Martin, Adduct removal from methanofullerenes reductive electrochemistry, *Chem. Commun.* 917–918 (2000).
- [19] R. Kessinger, N.S. Fender, L.E. Echegoyen, C. Thilgen, L. Echegoyen, F. Diederich, Selective electrolytic removal of bis(alkoxycarbonyl)methano addends from C_{60} *bis*-adducts and electrochemical stability of C_{70} derivatives, *Chem. Eur. J.* 6 (2000) 2184–2192.
- [20] O. Lukoyanova, C.M. Cardona, M. Altable, S. Filippone, Á. Martín Domenech, N. Martín, L. Echegoyen, Selective electrochemical retro-cycloaddition reaction of pyrrolidinofullerenes, *Angew. Chem. Int. Ed.* 45 (2006) 7430–7433.
- [21] R. Kessinger, J. Crassous, A. Herrmann, M. Rüttimann, L. Echegoyen, F. Diederich, Preparation of enantiomerically pure C_{76} with a general electrochemical method for the removal of di(alkoxycarbonyl)methano bridges from methanofullerenes: the retro-Bingel reaction, *Angew. Chem. Int. Ed.* 37 (1998) 1919–1922.
- [22] J.R. Heath, S.C. O'Brien, Q. Zhang, Y. Liu, R.F. Curl, F.K. Tittel, R.E. Smalley, Lanthanum complexes of spheroidal carbon shells, *J. Am. Chem. Soc.* 107 (1985) 7779–7780.
- [23] Y. Chai, T. Guo, C. Jin, R.E. Haufler, L.P.F. Chibante, J. Fure, L. Wang, J.M. Alford, R.E. Smalley, Fullerenes with metals inside, *J. Phys. Chem.* 95 (1991) 7564–7568.
- [24] S. Stevenson, G. Rice, T. Glass, K. Harich, F. Cromer, M.R. Jordan, J. Craft, E. Hadju, R. Bible, M.M. Olmstead, K. Maitra, A.J. Fisher, A.L. Balch, H.C. Dorn, Small-bandgap endohedral metallofullerenes in high yield and purity, *Nature* 402 (1999) 898.
- [25] F. Melin, M.N. Chaur, S. Engmann, B. Elliott, A. Kumbhar, A.J. Athans, L. Echegoyen, The large $\text{Nd}_3\text{N}@C_{2n}$ ($40 \leq n \leq 49$) cluster fullerene family: Preferential templating of a C_{88} cage by a trimetallic nitride cluster, *Angew. Chem. Int. Ed.* 46 (2007) 9032–9035.
- [26] T. Zuo, K. Walker, M.M. Olmstead, F. Melin, B.C. Holloway, L. Echegoyen, H.C. Dorn, M.N. Chaur, C.J. Chancellor, C.M. Beavers, A.L. Balch, A.J. Athans, New egg-shaped fullerenes: non-isolated pentagon structures of $\text{TM}_3\text{N}@C_{51}365\text{-C}_{84}$ and $\text{Gd}_3\text{N}@C_{51}365\text{-C}_{84}$, *Chem. Commun.* 1067–1069 (2008).
- [27] M.N. Chaur, F. Melin, B. Elliott, A. Kumbhar, A.J. Athans, L. Echegoyen, New $\text{M}_3\text{N}@C_{2n}$ endohedral metallofullerene families ($\text{M} = \text{Nd}, \text{Pr}, \text{Ce}$; $n = 40\text{--}53$): expanding the preferential templating of the C_{88} cage and approaching the C_{96} cage, *Chem. Eur. J.* 14 (2008) 4594–4599.
- [28] M.N. Chaur, F. Melin, J. Ashby, B. Elliott, A. Kumbhar, A.M. Rao, L. Echegoyen, Lanthanum nitride endohedral fullerenes $\text{La}_3\text{N}@C_{2n}$ ($43 \leq n \leq 55$): preferential formation of $\text{La}_3\text{N}@C_{96}$, *Chem. Eur. J.* 14 (2008) 8213–8219.
- [29] S. Steven, Preparation and Purification of Endohedral Metallofullerenes, Endohedral Metallofullerenes, CRC Press, 2014, pp. 19–66.
- [30] M. Alvaro, P. Atienzar, P. de la Cruz, J.L. Delgado, V. Troiani, H. García, F. Langa, A. Palkar, L. Echegoyen, Synthesis, photochemistry, and electrochemistry of single-wall carbon nanotubes with pendent pyridyl groups and of their metal complexes with zinc porphyrin. Comparison with pyridyl-bearing fullerenes, *J. Am. Chem. Soc.* 128 (2006) 6626–6635.
- [31] R. Valencia, A. Rodríguez-Fortea, A. Clotet, C. de Graaf, M.N. Chaur, L. Echegoyen, J.M. Poblet, Electronic structure and redox properties of metal nitride endohedral fullerenes $\text{M}_3\text{N}@C_{2n}$ ($\text{M} = \text{Sc}, \text{Y}, \text{La}$, and Gd ; $2n = 80, 84, 88, 92, 96$), *Chem. Eur. J.* 15 (2009) 10997–11009.
- [32] Y. Lian, Z. Shi, X. Zhou, Z. Gu, Different extraction behaviors between divalent and trivalent endohedral metallofullerenes, *Chem. Mater.* 16 (2004) 1704–1714.
- [33] T. Akasaka, X. Lu, Structural and electronic properties of endohedral metallofullerenes, *Chem. Rec.* 12 (2012) 256–269.
- [34] T. Tsuchiya, T. Wakahara, Y. Lian, Y. Maeda, T. Akasaka, T. Kato, N. Mizorogi, S. Nagase, Selective extraction and purification of endohedral metallofullerene from carbon soot, *J. Phys. Chem. B* 110 (2006) 22517–22520.
- [35] C. Yeretizian, J.B. Wiley, K. Holczer, T. Su, S. Nguyen, R.B. Kaner, R.L. Whetten, Partial separation of fullerenes by gradient sublimation, *J. Phys. Chem.* 97 (1993) 10097–10101.
- [36] J.W. Raebiger, R.D. Bolskar, Improved production and separation processes for gadolinium metallofullerenes, *J. Phys. Chem. C* 112 (2008) 6605–6612.
- [37] C.D. Angeli, T. Cai, J.C. Duchamp, J.E. Reid, E.S. Singer, H.W. Gibson, H.C. Dorn, Purification of trimetallic nitride templated endohedral metallofullerenes by a chemical reaction of congeners with eutectic 9-methylanthracene, *Chem. Mater.* 20 (2008) 4993–4997.
- [38] S. Stevenson, M.A. Mackey, C.E. Coumbe, J.P. Phillips, B. Elliott, L. Echegoyen, Rapid removal of D5h isomer using the “stir and filter approach” and isolation of large quantities of isomerically pure $\text{Sc}_3\text{N}@C_{80}$ metallic nitride fullerenes, *J. Am. Chem. Soc.* 129 (2007) 6072–6073.
- [39] S. Stevenson, K. Harich, H. Yu, R.R. Stephen, D. Heaps, C. Coumbe, J.P. Phillips, Nonchromatographic “stir and filter approach” (SAFA) for isolating $\text{Sc}_3\text{N}@C_{80}$ metallofullerenes, *J. Am. Chem. Soc.* 128 (2006) 8829–8835.
- [40] S. Stevenson, M.A. Mackey, J.E. Pickens, M.A. Stuart, B.S. Confait, J.P. Phillips, Selective complexation and reactivity of metallic nitride and oxometallic

- fullerenes with lewis acids and use as an effective purification method, *Inorg. Chem.* 48 (2009) 11685–11690.
- [41] M.E. Plonska-Brzezinska, A.J. Athans, J.P. Phillips, S. Stevenson, L. Echegoyen, A reinvestigation of the electrochemical behavior of $\text{Sc}_3\text{N@C}_{80}$, *J. Electroanal. Chem.* 614 (2008) 171–174.
 - [42] B. Elliott, L. Yu, L. Echegoyen, A simple isomeric separation of D5h and Ih $\text{Sc}_3\text{N@C}_{80}$ by selective chemical oxidation, *J. Am. Chem. Soc.* 127 (2005) 10885–10888.
 - [43] M.R. Cerón, F.-F. Li, L. Echegoyen, An efficient method to separate $\text{Sc}_3\text{N@C}_{80\text{Ih}}$ and D5h isomers and $\text{Sc}_3\text{N@C}_{78}$ by selective oxidation with acetylferrocenium $[\text{Fe}(\text{COCH}_3\text{C}_5\text{H}_4)\text{Cp}]^+$, *Chem. Eur. J.* 19 (2013) 7410–7415.
 - [44] H.W. Kroto, The stability of the fullerenes C_n , with $n = 24, 28, 32, 36, 50, 60$ and 70, *Nature* 329 (1987) 529–531.
 - [45] M.R. Cerón, F.-F. Li, L.A. Echegoyen, Endohedral fullerenes: the importance of electronic, size and shape complementarity between the carbon cages and the corresponding encapsulated clusters, *J. Phys. Org. Chem.* 27 (2014) 258–264.
 - [46] M. Garcia-Borras, S. Osuna, M. Swart, J.M. Luis, L. Echegoyen, M. Sola, Aromaticity as the driving force for the stability of non-IPR endohedral metallofullerene Bingel-Hirsch adducts, *Chem. Commun.* (2013).
 - [47] M. Garcia-Borras, S. Osuna, M. Swart, J.M. Luis, M. Sola, Maximum aromaticity as a guiding principle for the most suitable hosting cages in endohedral metallofullerenes, *Angew. Chem. Int. Ed.* 52 (2013) 9275–9278.
 - [48] M.R. Ceron, M. Izquierdo, N. Alegret, J.A. Valdez, A. Rodriguez-Forte, M.M. Olmstead, A.L. Balch, J.M. Poblet, L. Echegoyen, Reactivity differences of $\text{Sc}_3\text{N@C}_{2n}$ ($2n = 68$ and 80). Synthesis of the first methanofullerene derivatives of $\text{Sc}_3\text{N@D}_{5h}\text{-C}_{80}$, *Chem. Commun.* 52 (2016) 64–67.
 - [49] Y. Zhang, K.B. Ghiassi, Q. Deng, N.A. Samoylova, M.M. Olmstead, A.L. Balch, A. A. Popov, Synthesis and structure of $\text{LaSc}_2\text{N@Cs}(\text{hept})\text{-C}_{80}$ with one heptagon and thirteen pentagons, *Angew. Chem. Int. Ed.* 54 (2015) 495–499.
 - [50] M.M. Olmstead, A. de Bettencourt-Dias, J.C. Duchamp, S. Stevenson, D. Marciu, H.C. Dorn, A.L. Balch, Isolation and structural characterization of the endohedral fullerene $\text{Sc}_3\text{N@C}_{78}$, *Angew. Chem. Int. Ed.* 40 (2001) 1223–1225.
 - [51] J.M. Campanera, C. Bo, M.M. Olmstead, A.L. Balch, J.M. Poblet, Bonding within the endohedral fullerenes $\text{Sc}_3\text{N@C}_{78}$ and $\text{Sc}_3\text{N@C}_{80}$ as determined by density functional calculations and reexamination of the crystal structure of $[\text{Sc}_3\text{N@C}_{78}]\text{-Co}(\text{OEP})\cdot 1.5(\text{C}_6\text{H}_6)\cdot 0.3(\text{CHCl}_3)$, *J. Phys. Chem. A* 106 (2002) 12356–12364.
 - [52] M.M. Olmstead, H.M. Lee, J.C. Duchamp, S. Stevenson, D. Marciu, H.C. Dorn, A. L. Balch, $\text{Sc}_3\text{N@C}_{68}$: folded pentalene coordination in an endohedral fullerene that does not obey the isolated pentagon rule, *Angew. Chem. Int. Ed.* 42 (2003) 900–903.
 - [53] T. Cai, L. Xu, M.R. Anderson, Z. Ge, T. Zuo, X. Wang, M.M. Olmstead, A.L. Balch, H.W. Gibson, H.C. Dorn, Structure and enhanced reactivity rates of the D5h $\text{Sc}_3\text{N@C}_{80}$ and $\text{Lu}_3\text{N@C}_{80}$ metallofullerene isomers: the importance of the pyracylene motif, *J. Am. Chem. Soc.* 128 (2006) 8581–8589.
 - [54] B.Q. Mercado, M.N. Chaur, L. Echegoyen, J.A. Gharamaleki, M.M. Olmstead, A. L. Balch, A single crystal X-ray diffraction study of a fully ordered co-crystal of pristine $\text{Sc}_3\text{N@D}_{3h}(5)\text{-C}_{78}$, *Polyhedron* 58 (2013) 129–133.
 - [55] L.-H. Gan, J.-Q. Zhao, Q. Hui, Nonclassical fullerenes with a heptagon violating the pentagon adjacency penalty rule, *J. Comput. Chem.* 31 (2010) 1715–1721.
 - [56] X. Lu, L. Bao, T. Akasaka, S. Nagase, Recent progress in the chemistry of endohedral metallofullerenes, *Chem. Commun.* 50 (2014) 14701–14715.
 - [57] Z. Wenjun, C. Muqing, B. Lipiao, Y. Michio, Lu Xing, M.O. Marilyn, B.G. Kamran, L.B. Alan, NMR Spectroscopic and X-Ray Crystallographic Characterization of Endohedral Metallofullerenes, *Endohedral Metallofullerenes*, CRC Press, 2014, pp. 97–132.
 - [58] L. Dunsch, S. Yang, L. Zhang, A. Svitova, S. Oswald, A.A. Popov, Metal sulfide in a C82 fullerene cage: a new form of endohedral clusterfullerenes, *J. Am. Chem. Soc.* 132 (2010) 5413–5421.
 - [59] W. Cai, J. Murillo, L. Echegoyen, Endohedral clusterfullerenes: future perspectives, *ECS J. Solid State Sci. Technol.* 6 (2017) M3031–M3034.
 - [60] M.N. Chaur, F. Melin, B. Elliott, A.J. Athans, K. Walker, B.C. Holloway, L. Echegoyen, $\text{Gd}_3\text{N@C}_{2n}$ ($n = 40, 42$, and 44): remarkably low HOMO–LUMO gap and unusual electrochemical reversibility of $\text{Gd}_3\text{N@C}_{88}$, *J. Am. Chem. Soc.* 129 (2007) 14826–14829.
 - [61] B.Q. Mercado, C.M. Beavers, M.M. Olmstead, M.N. Chaur, K. Walker, B.C. Holloway, L. Echegoyen, A.L. Balch, Is the isolated pentagon rule merely a suggestion for endohedral fullerenes? The structure of a second egg-shaped endohedral fullerene- $\text{Gd}_3\text{N@C}_s(39663)\text{-C}_{82}$, *J. Am. Chem. Soc.* 130 (2008) 7854–7855.
 - [62] C.M. Beavers, M.N. Chaur, M.M. Olmstead, L. Echegoyen, A.L. Balch, Large metal ions in a relatively small fullerene cage: the structure of $\text{Gd}_3\text{N@C}_2(22010)\text{-C}_{78}$ departs from the isolated pentagon rule, *J. Am. Chem. Soc.* 131 (2009) 11519–11524.
 - [63] M. Mulet-Gas, A. Rodríguez-Forte, L. Echegoyen, J.M. Poblet, Relevance of thermal effects in the formation of endohedral metallofullerenes: the case of $\text{Gd}_3\text{N@Cs}(39663)\text{-C}_{82}$ and other related systems, *Inorg. Chem.* 52 (2013) 1954–1959.
 - [64] S. Stevenson, K.D. Arvola, M. Fahim, B.R. Martin, K.B. Ghiassi, M.M. Olmstead, A.L. Balch, Isolation and crystallographic characterization of $\text{Gd}_3\text{N@D}_{2(35)}\text{-C}_{88}$ through non-chromatographic methods, *Inorg. Chem.* 55 (2016) 62–67.
 - [65] S. Stevenson, J.P. Phillips, J.E. Reid, M.M. Olmstead, S.P. Rath, A.L. Balch, Pyramidalization of Gd_3N inside a C_{80} cage. The synthesis and structure of $\text{Gd}_3\text{N@C}_{80}$, *Chem. Commun.* (2004) 2814–2815.
 - [66] N. Chen, M.N. Chaur, C. Moore, J.R. Pinzon, R. Valencia, A. Rodríguez-Forte, J. M. Poblet, L. Echegoyen, Synthesis of a new endohedral fullerene family, $\text{Sc}_2\text{S@C}_{2n}$ ($n = 40\text{--}50$) by the introduction of SO_2 , *Chem. Commun.* 46 (2010) 4818–4820.
 - [67] B.Q. Mercado, N. Chen, A. Rodríguez-Forte, M.A. Mackey, S. Stevenson, L. Echegoyen, J.M. Poblet, M.M. Olmstead, A.L. Balch, The shape of the $\text{Sc}_2(\mu_2\text{-S})$ unit trapped in C_{82} : crystallographic, computational, and electrochemical studies of the isomers, $\text{Sc}_2(\mu_2\text{-S})\text{@C}_s(6)\text{-C}_{82}$ and $\text{Sc}_2(\mu_2\text{-S})\text{@C}_{3v}(8)\text{-C}_{82}$, *J. Am. Chem. Soc.* 133 (2011) 6752–6760.
 - [68] T. Wakahara, H. Nikawa, T. Kikuchi, T. Nakahodo, G.M.A. Rahman, T. Tsuchiya, Y. Maeda, T. Akasaka, K. Yoza, E. Horn, K. Yamamoto, N. Mizorogi, Z. Slanina, S. Nagase, La@C_{72} having a non-IPR carbon cage, *J. Am. Chem. Soc.* 128 (2006) 14228–14229.
 - [69] K. Ziegler, A. Mueller, K.Y. Amsharov, M. Jansen, Disclosure of the elusive $\text{C}_{2v}\text{-C}_{72}$ carbon cage, *J. Am. Chem. Soc.* 132 (2010) 17099–17101.
 - [70] Y.-Z. Tan, T. Zhou, J. Bao, G.-J. Shan, S.-Y. Xie, R.-B. Huang, L.-S. Zheng, $\text{C}_{72}\text{C}_{14}$: a pristine fullerene with favorable pentagon-adjacent structure, *J. Am. Chem. Soc.* 132 (2010) 17102–17104.
 - [71] X. Lu, H. Nikawa, T. Nakahodo, T. Tsuchiya, M.O. Ishitsuka, Y. Maeda, T. Akasaka, M. Toki, H. Sawa, Z. Slanina, N. Mizorogi, S. Nagase, Chemical understanding of a non-IPR metallofullerene: stabilization of encaged metals on fused-pentagon bonds in $\text{La}_2\text{@C}_{72}$, *J. Am. Chem. Soc.* 130 (2008) 9129–9136.
 - [72] N. Chen, C.M. Beavers, M. Mulet-Gas, A. Rodríguez-Forte, E.J. Munoz, Y.-Y. Li, M.M. Olmstead, A.L. Balch, J.M. Poblet, L. Echegoyen, $\text{Sc}_2\text{S@Cs}(10,528)\text{-C}_{72}$: a dimetallic sulfide endohedral fullerene with a non isolated pentagon rule cage, *J. Am. Chem. Soc.* 134 (2012) 7851–7860.
 - [73] N. Chen, M. Mulet-Gas, Y.-Y. Li, R.E. Stene, C.W. Atherton, A. Rodríguez-Forte, J.M. Poblet, L. Echegoyen, $\text{Sc}_2\text{S@C}_2(7892)\text{-C}_{70}$: a metallic sulfide cluster inside a non-IPR C_{70} cage, *Chem. Sci.* 4 (2013) 180–186.
 - [74] T. Yumura, Y. Sato, K. Suenaga, S. Iijima, Which do endohedral Ti_2C_{80} metallofullerenes prefer energetically: $\text{Ti}_2\text{@C}_{80}$ or $\text{Ti}_2\text{C}_{2}\text{@C}_{78}$? A theoretical study, *J. Phys. Chem. B* 109 (2005) 20251–20255.
 - [75] K. Tan, X. Lu, Ti_2C_{80} is more likely a titanium carbide endohedral metallofullerene ($\text{Ti}_2\text{C}_2\text{@C}_{78}$), *Chem. Commun.* (2005) 4444–4446.
 - [76] Y. Sato, T. Yumura, K. Suenaga, H. Moribe, D. Nishide, M. Ishida, H. Shinohara, S. Iijima, Direct imaging of intracage structure in titanium-carbide endohedral metallofullerene, *Phys. Rev. B* 73 (2006) 193401.
 - [77] B. Cao, K. Suenaga, T. Okazaki, H. Shinohara, Production, isolation, and EELS characterization of $\text{Ti}_2\text{@C}_{84}$ dititanium metallofullerenes, *J. Phys. Chem. B* 106 (2002) 9295–9298.
 - [78] S. Yang, C. Chen, A.A. Popov, W. Zhang, F. Liu, L. Dunsch, An endohedral titanium(III) in a cluster fullerene: putting a non-group-III metal nitride into the $\text{C}_{80}\text{-Ih}$ fullerene cage, *Chem. Commun.* (2009) 6391–6393.
 - [79] F.-F. Li, N. Chen, M. Mulet-Gas, V. Triana, J. Murillo, A. Rodríguez-Forte, J.M. Poblet, L. Echegoyen, $\text{Ti}_2\text{S@D}_{3h}(24,109)\text{-C}_{78}$: a sulfide cluster metallofullerene containing only transition metals inside the cage, *Chem. Sci.* 4 (2013) 3404–3410.
 - [80] C.-R. Wang, T. Kai, T. Tomiyama, T. Yoshida, Y. Kobayashi, E. Nishibori, M. Takata, M. Sakata, H. Shinohara, A scandium carbide endohedral metallofullerene: ($\text{Sc}_2\text{C}_2\text{@C}_{84}$), *Angew. Chem. Int. Ed.* 40 (2001) 397–399.
 - [81] Q. Deng, A.A. Popov, Clusters encapsulated in endohedral metallofullerenes: how strained are they?, *J. Am. Chem. Soc.* 136 (2014) 4257–4264.
 - [82] Y. Nishimoto, Z. Wang, K. Morokuma, S. Irie, Molecular and electronic structures of endohedral fullerenes, $\text{Sc}_2\text{C}_2\text{@C}_{3v}\text{-C}_{82}$ and $\text{Sc}_2\text{@C}_{3v}\text{-C}_{82}$: benchmark for SCC-DFTB and proposal of new inner cluster structures, *Phys. Status Solidi B* 249 (2012) 324–334.
 - [83] F. Liu, T. Wei, S. Wang, J. Guan, X. Lu, S. Yang, A Bent Tb_2C_2 Cluster Encaged in a $\text{C}_s(6)\text{-C}_{82}$ Cage: Synthesis, isolation and X-ray crystallographic study, fullerenes, nanotubes and carbon nanostructures, 22 (2014) 215–226.
 - [84] C.-H. Chen, K.B. Ghiassi, M.R. Cerón, M.A. Guerrero-Ayala, L. Echegoyen, M.M. Olmstead, A.L. Balch, Beyond the butterfly: $\text{Sc}_2\text{C}_2\text{@C}_{2v}(9)\text{-C}_{86}$, an endohedral fullerene containing a planar, twisted Sc_2C_2 unit with remarkable crystalline order in an unprecedented carbon cage, *J. Am. Chem. Soc.* 137 (2015) 10116–10119.
 - [85] C.-H. Chen, L. Abella, M.R. Cerón, M.A. Guerrero-Ayala, A. Rodríguez-Forte, M.M. Olmstead, X.B. Powers, A.L. Balch, J.M. Poblet, L. Echegoyen, Zigzag Sc_2C_2 carbide cluster inside a [88]fullerene cage with one heptagon, $\text{Sc}_2\text{C}_2\text{@Cs}(\text{hept})\text{-C}_{88}$: a kinetically trapped fullerene formed by C_2 insertion?, *J. Am. Chem. Soc.* 138 (2016) 13030–13037.
 - [86] P.W. Dunk, M. Mulet-Gas, Y. Nakanishi, N.K. Kaiser, A. Rodríguez-Forte, H. Shinohara, J.M. Poblet, A.G. Marshall, H.W. Kroto, Bottom-up formation of endohedral mono-metallofullerenes is directed by charge transfer, *Nat. Commun.* 5 (2014) 5844.
 - [87] C.M. Cardona, A. Kitaygorodskiy, A. Ortiz, M.Á. Herranz, L. Echegoyen, The first fulleropyrrolidine derivative of $\text{Sc}_3\text{N@C}_{80}$: pronounced chemical shift differences of the geminal protons on the pyrrolidine ring, *J. Org. Chem.* 70 (2005) 5092–5097.
 - [88] M.N. Chaur, R. Valencia, A. Rodríguez-Forte, J.M. Poblet, L. Echegoyen, Trimetallic nitride endohedral fullerenes: experimental and theoretical evidence for the $\text{M}_3\text{N}_6\text{+@C}_{2n6^-}$ model, *Angew. Chem. Int. Ed.* 48 (2009) 1425–1428.
 - [89] C.M. Cardona, A. Kitaygorodskiy, L. Echegoyen, Trimetallic nitride endohedral metallofullerenes: reactivity dictated by the encapsulated metal cluster, *J. Am. Chem. Soc.* 127 (2005) 10448–10453.

- [90] L. Echegoyen, C.J. Chancellor, C.M. Cardona, B. Elliott, J. Rivera, M.M. Olmstead, A.L. Balch, X-Ray crystallographic and EPR spectroscopic characterization of a pyrrolidine adduct of Y₃N@C₈₀, *Chem. Commun.* (2006) 2653–2655.
- [91] N. Chen, J.R. Pinzon, L. Echegoyen, Influence of the encapsulated clusters on the electrochemical behaviour of endohedral fullerene derivatives: comparative study of N-tritylpyrrolidino derivatives of Sc₃N@I(h)-C₈₀ and Lu₃N@I(h)-C₈₀, *ChemPhysChem* 12 (2011) 1422–1425.
- [92] A. Rodríguez-Fortea, J.M. Campanera, C.M. Cardona, L. Echegoyen, J.M. Poblet, Dancing on a fullerene surface: isomerization of Y₃N@(N-ethylpyrrolidino-C₈₀) from the 6,6 to the 5,6 regioisomer, *Angew. Chem. Int. Ed.* 45 (2006) 8176–8180.
- [93] S. Aroua, Y. Yamakoshi, Prato reaction of M₃N@I_h-C₈₀ (M = Sc, Lu, Y, Gd) with reversible isomerization, *J. Am. Chem. Soc.* 134 (2012) 20242–20245.
- [94] N. Chen, E.-Y. Zhang, K. Tan, C.-R. Wang, X. Lu, Size effect of encaged clusters on the exohedral chemistry of endohedral fullerenes: a case study on the pyrrolidino reaction of Sc_xGd_{3-x}N@C₈₀ (x = 0–3), *Org. Lett.* 9 (2007) 2011–2013.
- [95] M. Chen, X. Lu, M.R. Cerón, M. Izquierdo, L. Echegoyen, Chemistry of conventional endohedral metallofullerenes and cluster endohedral fullerenes, in: X. Lu, L. Echegoyen, A.L. Balch, S. Nagase, T. Akasaka (Eds.), *Endohedral Metallofullerenes: Basic and Applications*, CRC Press, 2014, pp. 173–210.
- [96] N. Martín, M. Altale, S. Filippone, A. Martín-Domenech, L. Echegoyen, C.M. Cardona, Retro-cycloaddition reaction of pyrrolidinofullerenes, *Angew. Chem. Int. Ed.* 45 (2006) 110–114.
- [97] O. Lukoyanova, C.M. Cardona, M. Altale, S. Filippone, A. Martín Domenech, N. Martín, L. Echegoyen, Selective electrochemical retro-cycloaddition reaction of pyrrolidinofullerenes, *Angew. Chem. Int. Ed.* 45 (2006) 7430–7433.
- [98] O. Lukoyanova, C.M. Cardona, J. Rivera, L.Z. Lugo-Morales, C.J. Chancellor, M. M. Olmstead, A. Rodríguez-Fortea, J.M. Poblet, A.L. Balch, L. Echegoyen, “Open rather than closed” malonate methano-fullerene derivatives. the formation of methanofulleroid adducts of Y₃N@C₈₀, *J. Am. Chem. Soc.* 129 (2007) 10423–10430.
- [99] N. Alegret, M.N. Chaur, E. Santos, A. Rodríguez-Fortea, L. Echegoyen, J.M. Poblet, Bingel-Hirsch reactions on non-IPR Gd₃N@C_{2n} (2n = 82 and 84), *J. Org. Chem.* 75 (2010) 8299–8302.
- [100] J.R. Pinzon, T. Zuo, L. Echegoyen, Synthesis and electrochemical studies of Bingel-Hirsch derivatives of M₃N@I_h-C₈₀ (M = Sc, Lu), *Chem. Eur. J.* 16 (2010) 4864–4869. S4864/4861–S4864/4815.
- [101] M. García-Borràs, M.R. Cerón, S. Osuna, M. Izquierdo, J.M. Luis, L. Echegoyen, M. Solà, The regioselectivity of Bingel-Hirsch cycloadditions on isolated pentagon rule endohedral metallofullerenes, *Angew. Chem. Int. Ed.* 55 (2016) 2374–2377.
- [102] M.N. Chaur, F. Melin, A.J. Athans, B. Elliott, K. Walker, B.C. Holloway, L. Echegoyen, The influence of cage size on the reactivity of trimetallic nitride metallofullerenes: a mono- and bis-methanoadduct of Gd₃N@C₈₀ and a monoadduct of Gd₃N@C₈₄, *Chem. Commun.* (2008) 2665–2667.
- [103] D.M. Rivera-Nazario, J.R. Pinzón, S. Stevenson, L.A. Echegoyen, Buckyball maracas: exploring the inside and outside properties of endohedral fullerenes, *J. Phys. Org. Chem.* 26 (2013) 194–205.
- [104] F.-F. Li, A. Rodríguez-Fortea, J.M. Poblet, L. Echegoyen, Reactivity of metallic nitride endohedral metallofullerene anions: electrochemical synthesis of a Lu₃N@I_h-80 derivative, *J. Am. Chem. Soc.* 133 (2011) 2760–2765.
- [105] F.-F. Li, A. Rodríguez-Fortea, P. Peng, C.G.A. Campos, J.M. Poblet, L. Echegoyen, Electrosynthesis of a Sc₃N@I_h-C₈₀ methano derivative from trianionic Sc₃N@I_h-C₈₀, *J. Am. Chem. Soc.* 134 (2012) 7480–7487.
- [106] R.B. Ross, C.M. Cardona, D.M. Guldi, S.G. Sankaranarayanan, M.O. Reese, N. Kopidakis, J. Peet, B. Walker, G.C. Bazan, E. Van Keuren, B.C. Holloway, M. Drees, Endohedral fullerenes for organic photovoltaic devices, *Nat. Mater.* 8 (2009) 208–212.
- [107] I. Riedel, E. von Hauff, J. Parisi, N. Martín, F. Giacalone, V. Dyakonov, Diphenylmethanofullerenes: new and efficient acceptors in bulk-heterojunction solar cells, *Adv. Funct. Mater.* 15 (2005) 1979–1987.
- [108] A. Sánchez-Díaz, M. Izquierdo, S. Filippone, N. Martín, E. Palomares, The origin of the high voltage in DPM12/P3HT organic solar cells, *Adv. Funct. Mater.* 20 (2010) 2695–2700.
- [109] H.J. Bolink, E. Coronado, A. Forment-Aliaga, M. Lenes, A. La Rosa, S. Filippone, N. Martín, Polymer solar cells based on diphenylmethanofullerenes with reduced sidechain length, *J. Mater. Chem.* 21 (2011) 1382–1386.
- [110] C.J. Brabec, A. Cravino, D. Meissner, N.S. Sariciftci, T. Fromherz, M.T. Rispens, L. Sanchez, J.C. Hummelen, Origin of the open circuit voltage of plastic solar cells, *Adv. Funct. Mater.* 11 (2001) 374–380.
- [111] K. Sun, Z. Xiao, S. Lu, W. Zajackowski, W. Pisula, E. Hanssen, J.M. White, R.M. Williamson, J. Subbiah, J. Ouyang, A.B. Holmes, W.W.H. Wong, D.J. Jones, A molecular nematic liquid crystalline material for high-performance organic photovoltaics, *Nat. Commun.* 6 (2015).
- [112] M. Izquierdo, M.R. Cerón, M.M. Olmstead, A.L. Balch, L. Echegoyen, [5,6]-Open methanofullerene derivatives of I_h-C₈₀, *Angew. Chem. Int. Ed.* 52 (2013) 11826–11830.
- [113] J.R. Pinzon, M.E. Plonska-Brzezinska, C.M. Cardona, A.J. Athans, S.S. Gayathri, D.M. Guldi, M.A. Herranz, N. Martín, T. Torres, L. Echegoyen, Sc₃N@C₈₀-ferrocene electron-donor/acceptor conjugates as promising materials for photovoltaic applications, *Angew. Chem. Int. Ed.* 47 (2008) 4173–4176.
- [114] L.P. Hernandez-Eguia, E.C. Escudero-Adan, J.R. Pinzon, L. Echegoyen, P. Ballester, Complexation of Sc₃N@C₈₀ endohedral fullerene with cyclic Zn-bisporphyrins: solid state and solution studies, *J. Org. Chem.* 76 (2011) 3258–3265.
- [115] C. Shu, W. Xu, C. Slebodnick, H. Champion, W. Fu, J.E. Reid, H. Azurmendi, C. Wang, K. Harich, H.C. Dorn, H.W. Gibson, Syntheses and structures of phenyl-C₈₁-butyric acid methyl esters (PCBMs) from M₃N@C₈₀, *Org. Lett.* 11 (2009) 1753–1756.
- [116] M. Rudolf, S. Wolfrum, D.M. Guldi, L. Feng, T. Tsuchiya, T. Akasaka, L. Echegoyen, Endohedral metallofullerenes-filled fullerene derivatives towards multifunctional reaction center mimics, *Chem. Eur. J.* 18 (2012) 5136–5148.
- [117] M.R. Cerón, M. Izquierdo, M. García-Borràs, S.S. Lee, S. Stevenson, S. Osuna, L. Echegoyen, Bis-1,3-dipolar cycloadditions on endohedral fullerenes M₃N@I_h-C₈₀ (M = Sc, Lu): remarkable endohedral-cluster regiochemical control, *J. Am. Chem. Soc.* 137 (2015) 11775–11782.
- [118] S. Aroua, M. García-Borràs, M.F. Böltér, S. Osuna, Y. Yamakoshi, Endohedral metal-induced regioselective formation of bis-Prato adduct of Y₃N@I_h-C₈₀ and Gd₃N@I_h-C₈₀, *J. Am. Chem. Soc.* 137 (2015) 58–61.
- [119] A. Mishra, P. Bäuerle, Small molecule organic semiconductors on the move: promises for future solar energy technology, *Angew. Chem. Int. Ed.* 51 (2012) 2020–2067.
- [120] M.R. Cerón, L. Echegoyen, Recent progress in the synthesis of regio-isomerically pure bis-adducts of empty and endohedral fullerenes, *J. Phys. Org. Chem.* 29 (2016) 613–619.
- [121] M.R. Cerón, M. Izquierdo, A. Aghabali, J.A. Valdez, K.B. Ghiassi, M.M. Olmstead, A.L. Balch, F. Wudl, L. Echegoyen, Tethered bisadducts of C₆₀ and C₇₀ with addends on a common hexagonal face and a 12-membered hole in the fullerene cage, *J. Am. Chem. Soc.* 137 (2015) 7502–7508.
- [122] M.R. Cerón, M. Izquierdo, Y. Pi, S.L. Atehortúa, L. Echegoyen, Tether-directed bisfunctionalization reactions of C₆₀ and C₇₀, *Chem. Eur. J.* 21 (2015) 7881–7885.
- [123] M. Izquierdo, M.R. Cerón, N. Alegret, A.J. Metta-Magana, A. Rodríguez-Fortea, J.M. Poblet, L. Echegoyen, Unexpected isomerism in *cis*-2 bis(pyrrolidino) [60]fullerene diastereomers, *Angew. Chem. Int. Ed.* 52 (2013) 12928–12931.
- [124] M.N. Chaur, F. Melin, A.L. Ortiz, L. Echegoyen, Chemical, electrochemical, and structural properties of endohedral metallofullerenes, *Angew. Chem. Int. Ed.* 48 (2009) 7514–7538.
- [125] S. Stevenson, K. Harich, H. Yu, R.R. Stephen, D. Heaps, C. Coumbe, J.P. Phillips, Nonchromatographic “stir and filter approach” (SAFA) for isolating Sc₃N@C-80 metallofullerenes, *J. Am. Chem. Soc.* 128 (2006) 8829–8835.
- [126] S. Stevenson, M.A. Mackey, C.E. Coumbe, J.P. Phillips, B. Elliott, L. Echegoyen, Rapid removal of D-5h isomer using the “stir and filter approach” and isolation of large quantities of isomerically pure Sc₃N@C-80 metallic nitride fullerenes, *J. Am. Chem. Soc.* 129 (2007) 6072–6073.
- [127] S. Stevenson, C.B. Rose, A.A. Robson, D.T. Heaps, J.P. Buchanan, Effect of water and solvent selection on the SAFA purification times for metallic nitride fullerenes, Fullerenes, Nanotubes, Carbon Nanostruct. 22 (2014) 182–189.



Lawrence Livermore National Laboratories, in the material science division.



novel technology platforms based on carbon nanomaterials for molecular imaging, photodynamic therapy and targeted nano-therapeutics towards the development of biosensors and healthcare-devices.

Maira R. Cerón was born in Pasto, Nariño, Colombia, in 1989. In 2010, she graduated as a Magna Cum Laude from her BSc in Chemistry at Universidad del Valle, Cali, Colombia, where she was involved in the synthesis of organometallic compounds and their electrochemical characterization. She received her PhD (2015) in Chemistry at the University of Texas at El Paso, under the supervision of Prof. Luis Echegoyen. Her research was mainly focus in the synthesis, spectroscopic and electrochemical characterization of *mono*- and *bis*-derivatives of empty and endohedral fullerenes. She is currently a postdoctoral research staff member at

Viviana Maffei graduated from University of Pavia, Italy in 2014 with a degree in Pharmacy. During her undergraduate studies, she participated in an Erasmus project at University College London, UK (Prof. Vittorio Bellotti's Group). She is currently getting her PhD in Sciences and Technologies of Chemistry and Materials at Istituto Italiano di Tecnologia in Genoa, Italy, under the supervision of Prof. Silvia Giordani. She was a summer intern at the University of Texas at El Paso (Prof. Luis Echegoyen's Group) and Trinity College Dublin (Prof. Eoin Scanlan's Group). Her current research projects involve the design and synthesis of



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.



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 Rio 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.