SYNTHESIS OF TRIMETALLIC NITRIDE ENDOHEDRAL METALLOFULLERENE DERIVATIVES FOR ENHANCED SOLAR ENERGY CONVERSION

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SYNTHESIS OF TRIMETALLIC NITRIDE ENDOHEDRAL METALLOFULLERENE DERIVATIVES FOR ENHANCED SOLAR ENERGY CONVERSION

A Dissertation
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Chemistry

by
Julio Roberto Pinzón Joya
December 2010

Accepted by:
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Dr. Luis Echegoyen
ABSTRACT

The preparation and electrochemical properties of donor – acceptor systems based on trimetallic nitride endohedral metallofullerenes (TNT-EMFs) for enhanced solar energy conversion is described. It was found that TNT-EMFs have an enhanced ability to stabilize charge separated states formed upon light irradiation when compared to empty cage fullerene analogues. The influence of the linker connecting the donor and acceptor moieties was studied in two different systems. Optimal conditions for preparing cyclopropanated Bingel-Hirsch derivatives of the most common TNT-EMFs were found; this functionalization approach is a very useful alternative to the 1,3-dipolar cycloaddition reactions that yield pyrrolidine derivatives, because the latter are sensitive to both heat and oxidation.

Novel D-A systems were prepared using this strategy and their electrochemical properties revealed that they form films by electro-oxidative polymerization. These films generate current under irradiation. Finally, the arcing conditions for the preparation of a novel sulfur endohedral metallofullerene family were optimized and their electrochemical properties were studied. Due to the high yields obtained, these new endohedral compounds may also be potential candidates to be used in similar applications to those found for other TNT-EMFs.
DEDICATION

This work is dedicated to my father for showing me the wonder of running our home on solar energy; to my mother for her unconditional support and love. To my brothers for keeping everything in order back home and to my little nieces, for all the joy and happiness they have brought to my life.
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Second I want to acknowledge all my Professors and classmates for making the Clemson experience an enjoyable one, to my friend Sabina Wang and her daughter Helina for being the best roommates ever, to my parents, my brothers and my girlfriend for their unconditional support and encouragement to pursue my degree.

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CHAPTER ONE

INTRODUCTION

With the growing demand for renewable sources for generating electricity, organic solar cells are perhaps the most promising technology to reduce prices and to improve the ease of manufacture of the solar panels for mass production. In this chapter, the discovery, preparation, reactivity, electrochemical properties, and the potential application of trimetallic nitride endohedral metallofullerenes (TNT-EMFs) in the construction of organic solar cells will be discussed. Some of the ideas in this introduction were published in Chapter 9 of the book “Chemistry of Nanocarbons”, edited by Akasaka, T., Wuld, F. and Nagase, S., Eds.; Wiley: USA, 2010; , pp 528 that I coauthored.

1. Trimetallic Nitride Endohedral Metallofullerenes (TNT-EMFs)

$\text{Sc}_3\text{N@I}_h\text{-C}_{80}$, the first member of the TNT-EMFs family,\textsuperscript{1} was discovered when a small amount of nitrogen was inadvertently introduced in the Krätschmer – Huffman reactor used for the preparation of fullerenes.\textsuperscript{2} The preparation of fullerenes with encapsulated metals had caught the attention of the scientific community because of the remarkable properties arising from the formal charge transfer from the encapsulated metal towards the fullerene cage.\textsuperscript{3} However, until the TNF-EMF family was discovered, other metallofullerene species were obtained in extremely low yields.\textsuperscript{4,5} Hence the discovery of $\text{Sc}_3\text{N@C}_{80}$ is considered a breakthrough because these metallofullerenes can
be prepared today in kilogram quantities and a variety of new applications in materials science have been suggested. Until today, TNT-EMFs containing Sc, Y, La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, Tm, Ti and Lu as single metal clusters or combinations of them with cages sizes ranging from C\textsubscript{68} up to C\textsubscript{104} have been reported.\textsuperscript{7-9} Illustrative examples of empty cage fullerenes (ECFs), classical endohedral metallofullerenes (EMFs) and trimetallic nitride endohedral metallofullerenes (TNT-EMFs) are shown in Figure 1.1.

![Figure 1.1 Examples of different fullerene families](image)

(a) Empty cage fullerene (ECF) (b) Classical endohedral metallofullerene (c) Trimetallic nitride endohedral metallofullerene (TNT-EMF)

1.1. Preparation and purification

The early preparation methods for M\textsubscript{3}N@C\textsubscript{2n} involved arcing graphite rods packed with metal oxides and graphite in a 1-3 Torr N\textsubscript{2}/300 Torr He atmosphere.\textsuperscript{1} After extracting the resulting soot in a Soxhlet apparatus using CS\textsubscript{2}/Toluene/Xylenes the resulting extract is washed with acetone in order to remove the polyaromatic hydrocarbons from the fullerenes. Once the fullerene mixture is dried, it is re-dissolved again in CS\textsubscript{2}/Toluene/Xylenes and separated by HPLC.\textsuperscript{10} A few years after the discovery of TNT-EMFs, Dunsch and collaborators suggested the use of alternative sources of nitrogen. CaNCN was initially used without too much success but the introduction of
NH₃ gas as the source of nitrogen yielded TNT-EMFs as the majority components of the raw fullerene extract. The reason for the success of the NH₃ reactive atmosphere method is that the more reactive empty cage fullerenes (ECFs) are destroyed by the ammonia gas. Further increases of the yields can be obtained if Cu is added to the graphite/metal oxide mixture and the rods are annealed at 1000 °C under a nitrogen atmosphere before the arcing process. A combination of the reactive atmosphere concept and the yield increase observed after adding copper led to the development of the “Chemically Adjusting Plasma Temperature, Energy, and Reactivity” (CAPTEAR) method, which produces the highest yield reported so far. In this method the graphite rods are packed with a mixture of graphite, metal oxide and Cu(NO₃)₂·2.5H₂O. The rods are not annealed but directly arced under a dynamic air atmosphere (6 Torr/min) that prevents the reactor pressure to rise to dangerous levels as a consequence of the gases that result from the decomposition of Cu(NO₃)₂·2.5H₂O. These gases suppress the formation of ECFs while helping to tune the reaction conditions in the plasma.

The first purification method used for the separation of TNT-EMFs was HPLC. However, this method is time consuming and large quantities of high purity solvents are required. The same reactivity difference that was used for the selective preparation of TNT-EMFs was later applied to develop simplified purification methods. Dorn and collaborators reported the utilization of a cyclopentadiene functionalized resin to separate the TNT-EMFs from ECFs in a single step. The more reactive ECFs react with the immobilized cyclopentadiene groups to yield Diels-Alder adducts, whereas the less reactive TNT-EMFs elute quickly through the column. A similar methodology based on
the Diels-Alder differential reactivity uses 9-methylanthracene. In this method the crude soot extract is reacted with eutectic 9-methylanthracene that yields a mixture of empty cage fullerene adducts and unreacted TNT-EMFs that are separated on a silica gel column.\textsuperscript{15} A very convenient non chromatographic method that is called “Stir and Filter Approach” (SAFA) involves the reaction of the soot extracts with amino-capped silica.\textsuperscript{16} The ECFs are bound to the silica by the amino groups while the less reactive TNT-EMFs remain in solution. This method is easily scalable and allows the preparation of gram amounts of TNT-EMFs.

The most studied TNT-EMFs are the ones with the trimetallic nitride clusters encapsulated in C\textsubscript{80} carbon cages although recently larger fullerene cages containing Nd, Pr, Ce and La have been reported.\textsuperscript{7} There are seven possible C\textsubscript{80} cages (D\textsubscript{2}, D\textsubscript{5h}, C\textsubscript{2v}, C\textsubscript{1}\textsubscript{2v}, D\textsubscript{3}, D\textsubscript{5h}, I\textsubscript{h}) that obey the isolated pentagon rule, which states that two consecutive pentagons cannot exist in a fullerene cage; \textsuperscript{17} two of them (D\textsubscript{5h} and I\textsubscript{h}) have been observed experimentally as TNT-EMF structures.\textsuperscript{18,19} The separation of these constitutional isomers of TNT-EMFs has been possible as well. The first method used was a linear combination of HPLC columns.\textsuperscript{18,19} Since the D\textsubscript{5h}-C\textsubscript{80} isomers are more reactive than the I\textsubscript{h}-C\textsubscript{80} ones, when a solution containing an isomeric mixture of M\textsubscript{3}N@C\textsubscript{80} fullerenes (D\textsubscript{5h} and I\textsubscript{h}) is stirred with amino-capped silica (SAFA method),\textsuperscript{16} the more reactive D\textsubscript{5h} isomer is bound to the silica, thus leaving the I\textsubscript{h} isomer in solution. Alternatively, TNT-EMF isomers can be separated based on their very different redox potentials. Ecchegoyen and collaborators reported the selective isolation of Sc\textsubscript{3}N@I\textsubscript{h}-C\textsubscript{80} after reacting the isomeric mixture with tris(4-bromophenyl)aminium hexachloro...
antimonate, which selectively oxidizes the most reactive $D_{5h}$ isomer. Finally a selective precipitation scheme based on Lewis acids that selectively complex TNT-EMFs, allows the separation and purification of pure isomers in gram quantities.

1.2. Reactivity

In classical ECFs (C$_{60}$, C$_{70}$, C$_{84}$, etc.) the reactivity is mainly driven by two factors: the strain resulting from the deviation from planarity expressed as the pyramidalization angle$^{22-24}$ and the electronic factors.$^{25}$ A lot of the strain energy is released after the carbon atoms participate in a chemical reaction and change their hybridization from sp$^2$ to sp$^3$. The second factor is important because fullerenes are fairly electronegative molecules with very rich redox chemistry and capable of accepting multiple electrons upon chemical reduction.$^{26}$ Very few chemical reactions have been reported on TNT-EMFs mostly as a result of their low availability. However, it has been observed that the reactivity of TNT-EMFs is influenced by the trapped metal and the symmetry of the carbon cage.$^{27}$ Similarly to what has been observed with ECFs, the main driving force controlling the reactivity of TNT-EMFs is the release of strain energy. However, the pyramidalization angle and the electronic properties of different carbons are affected by the nature of the encapsulated cluster.$^{28}$

Figure 1.2. Main C$_{80}$ carbon cages that encapsulate trimetallic nitride clusters. (a) $I_h$ isomer (b) $D_{5h}$ isomer (top view) (c) $D_{5h}$ isomer (front view)
As mentioned before the most abundant TNT-EMF species are encapsulated in \( \text{C}_{80} \) carbon cages (See Figure 1.2). In the \( I_{h}-\text{C}_{80} \) isomer (Figure 1.2a) there are two different types of carbons; 20 pyrene type carbons and 60 corannulene type carbons. There are two types of bonds in the \( I_{h}-\text{C}_{80} \) cage: the \([6,6]\) bonds which are between two six membered rings linking a pyrene type and a corannulene type carbon and the \([5,6]\) bonds which are between a five and a six membered rings linking two corannulene type carbons. The \( D_{5h} \) isomer, on the other hand, has 6 different types of carbon atoms and 9 types of bonds (See Figure 1.2b or Figure 1.2c).

The first reported example of a TNT-EMF derivative was a Diels-Alder adduct.\(^{29,30}\) This compound was prepared by the reaction between \(^{13}\text{C}\) labeled 6,7-dimethoxyisochroman-3-one and \( \text{Sc}_{3}\text{N}@I_{h}-\text{C}_{80} \). This cycloaddition reaction occurred regioselectively on a \([5,6]\) bond as corroborated both by NMR and X-ray crystal analysis. The next reaction reported for TNT-EMFs was the addition of azomethine ylides; also known as the Prato reaction.\(^{31}\) The compounds prepared were the \( N\)-ethylpyrrolidine-\([5,6]\)-\( \text{Sc}_{3}\text{N}@I_{h}-\text{C}_{80} \) and \( N\)-methylpyrrolidine-\([5,6]\)-\( \text{Sc}_{3}\text{N}@I_{h}-\text{C}_{80} \).\(^{32,33}\) Typically the 1,3 dipolar intermediate is generated by the reaction between an aldehyde and a glycine. However, it has been shown that in the case of \( \text{Sc}_{3}\text{N}@I_{h}-\text{C}_{80} \) and \( \text{Lu}_{3}\text{N}@I_{h}-\text{C}_{80} \) the reaction works in the absence of the aldehyde, but no explanation is offered regarding the formation of the azomethine ylide intermediate.\(^{34}\) In both cases the addition occurred regioselectively on a \([5,6]\) bond. However, the same reaction with \( \text{Y}_{3}\text{N}@I_{h}-\text{C}_{80} \) and \( \text{Er}_{3}\text{N}@I_{h}-\text{C}_{80} \) produced initially the \([6,6]\) regioisomer that was isomerized to the \([5,6]\) regioisomer upon heating,\(^{27}\) showing a pronounced influence of the encapsulated metal
on the regioselectivity of the addition. A more interesting case is the reaction between \( \text{N-trityl-5-oxazolidinone} \) and \( \text{Sc}_3\text{N}@I_h\text{-C}_{80} \) because it produces a mixture of the two regioisomers and as in the other cases, the [6,6] regioisomer (See Figure 1.3b) transforms to the [5,6] upon heating (See Figure 1.3a). The \( \text{N-tritylpyrroldino-[6,6]-Sc}_3\text{N}@I_h\text{-C}_{80} \) derivative is so far the only example of a [6,6] pyrroldine derivative of \( \text{Sc}_3\text{N}@I_h\text{-C}_{80}. \)

![Figure 1.3](image.png)

Figure 1.3. \( \text{N-tritylpyrroldine derivatives of Sc}_3\text{N}@C_{80} \) isomers. Under each isomer the bond and the patch where the reaction occurred is shown (a) 5,6 addition on the \( I_h \) carbon cage (b) 6,6 addition on the \( I_h \) carbon cage (c) Major product on the \( D_{5h} \) carbon cage (addition on a pyracylene patch) (d) Second major isomer (addition on a pyrene patch)

The same reaction was studied with the \( \text{Sc}_3\text{N}@D_{5h}\text{-C}_{80} \) isomer. The reaction with \( \text{Sc}_3\text{N}@D_{5h}\text{-C}_{80} \) is faster, indicating a higher reactivity. Despite the lower symmetry of the \( D_{5h} \) isomer, there are two predominant monoadducts, both possessing highly symmetric environments, as judged by \( ^1\text{H} \) NMR spectroscopy. Out of the nine different types of bonds there are only two of them that can yield highly symmetric products; the ones formed by carbons number 5 in Figure 1.2b or Figure 1.2c and the ones formed by the carbons number 6 in Figure 1.2b or Figure 1.2c. They produce the \( \text{N-tritylpyrroldines} \) shown in Figure 1.3c and Figure 1.3d, respectively. The isomer shown in Figure 1.3c is
the major component because the addition occurs on a pyracylene patch, which resembles the C\textsubscript{60} fullerene. A comparative study of the reactivity of the series Sc\textsubscript{3-x}Y\textsubscript{x}N@I\textsubscript{h}-C\textsubscript{80} showed a change of regioselectivity from [5,6] to [6,6] induced by the encapsulated metals.\textsuperscript{37} The same study with the Sc\textsubscript{3}Gd\textsubscript{3-x}N@C\textsubscript{80} series showed identical behavior, but [6,6]-Gd\textsubscript{3}N@I\textsubscript{h}-C\textsubscript{80} does not isomerize to the [5,6] isomer upon heating.\textsuperscript{38} The [6,6]-isomer is the preferred addition site because of the increased pyramidalization degree of the pyrene type carbon when the size of the cluster is increased.\textsuperscript{39}

Figure 1.4. Small cage TNT-EMFs (a) Sc\textsubscript{3}N@D\textsubscript{3h}-C\textsubscript{78} (b) Sc\textsubscript{3}N@D\textsubscript{3}-C\textsubscript{68}

Sc\textsubscript{3}N@D\textsubscript{3h}-C\textsubscript{78} and Sc\textsubscript{3}N@D\textsubscript{3}-C\textsubscript{68} (See Figure 1.4) are also formed during the preparation of Sc\textsubscript{3}N@C\textsubscript{80}. The same reaction with Sc\textsubscript{3}N@D\textsubscript{3h}-C\textsubscript{78} (78:5), which has 8 different types of carbons and 13 different types of bonds (See Figure 1.4a) and the Sc atoms are permanently coordinated to the 3 pyracylene patches,\textsuperscript{40} produce mainly two regioisomers, namely the addition product on the bond between carbons 3 and 5, and the one on the bond between carbons 2 and 4 in Figure 1.4a as shown by NMR and X-ray crystallography.\textsuperscript{41} The pyrrolidine adducts formed by TNT-EMFs are not thermally stable and decompose easily upon heating,\textsuperscript{42} even in the absence of a catalyst, or by
electrooxidative processes.\textsuperscript{43} This behavior may be useful for protecting/deprotecting strategies for functionalization of TNT-EMFs.

Free radical and nucleophilic additions have also been studied on TNT-EMFs. Sc$_3$N@$_{Ih}$-C$_{80}$ when refluxed in toluene in the presence of Na produces anionic species that precipitate out of the solution. These anionic species when reacted with water and exposed to air produce a mixture of water soluble compounds with general formula Sc$_3$N@C$_{80}$(OH)$_{10}$O$_{10}$, deduced from the X-ray photoelectron spectroscopy (XPS).\textsuperscript{44} In another example of free radical reactions, Sc$_3$N@$_{Ih}$-C$_{80}$ and 1,1,2,2-tetramesityl-1,2-disilirane were reacted both under UV irradiation and under thermal conditions but only the photochemical reaction was observed to occur. This behavior differs from that of La$_2$@$_{Ih}$-C$_{80}$ (a classical metallofullerene) where the reaction occurs both photochemically and thermally and constitutes another example of differences in reactivity of the fullerene cage due to the influence of the internal cluster.\textsuperscript{45,46} Two products were obtained from this reaction, a 1,2 addition product on a [5,6] bond and a 1,4-addition product where the addends were connected to corannulene type carbons. It was found that the 1,2 addition product converts to the 1,4 upon heating.

There are other examples of free radical reactions involving TNT-EMFs. The trifluoromethylation of an isomeric mixture of Sc$_3$N@$_{Ih}$-C$_{80}$ and Sc$_3$N@$_{D_{5h}}$-C$_{80}$ produced the 1,4 addition product on the $I_{h}$-C$_{80}$, following exactly the same pattern as the disiliranes case, while the $D_{5h}$-C$_{80}$ cage yielded the product with the addends connected to carbons number 4 in Figure 1.2b or Figure 1.2c.\textsuperscript{47} On the other hand, the reaction of Sc$_3$N@$_{Ih}$-C$_{80}$ or Lu$_3$N@$_{Ih}$-C$_{80}$ with benzyl bromide under UV irradiation produced the
bis benzyl-1,4 addition products\textsuperscript{48} further confirming the 1,4 addition pattern observed until now.

The Bingel-Hirsch reaction,\textsuperscript{49,50} a very useful functionalization strategy to prepare cyclopropanated fullerene derivatives, has also been used with TNT-EMFs, but in the latter cases this reaction produces open cage derivatives. When this reaction was attempted with Y\textsubscript{3}N@I\textsubscript{h}-C\textsubscript{80} under the same conditions as those used with C\textsubscript{60} it yielded the [6,6] monoadduct as the only product,\textsuperscript{27,51} but it failed with Sc\textsubscript{3}N@I\textsubscript{h}-C\textsubscript{80}. However, the reaction between Sc\textsubscript{3}N@I\textsubscript{h}-C\textsubscript{80} or Lu\textsubscript{3}N@I\textsubscript{h}-C\textsubscript{80} and diethyl-2-bromomalonate in the presence of Manganese(III) acetate to catalyze the formation of free radicals\textsuperscript{52} yields open cage fullerene derivatives or “fulleroids” on the [6,6] position as well. In chapter 4 our experimental design and success in the preparation of Bingel-Hirsch derivatives with Sc\textsubscript{3}N@I\textsubscript{h}-C\textsubscript{80} and Lu\textsubscript{3}N@I\textsubscript{h}-C\textsubscript{80} will be discussed.

The Bingel-Hirsch reaction on Sc\textsubscript{3}N@D\textsubscript{3h}-C\textsubscript{78} and Sc\textsubscript{3}N@D\textsubscript{3}-C\textsubscript{68} proceeds with remarkable regioselectivity.\textsuperscript{53} In the case of Sc\textsubscript{3}N@D\textsubscript{3h}-C\textsubscript{78} a monoadduct, where the addend was attached to the bond between carbons 3 and 5 was obtained. This monoadduct exhibits the same regioselectivity as that observed for the 1,3-dipolar cycloaddition reaction.\textsuperscript{41} A bisadduct was also obtained and the second addend was attached to the anti-1 position, which corresponds to the kinetically preferred site for nucleophilic attack\textsuperscript{54} (See Figure 1.5), in total agreement with the theoretically predicted regiochemistry.\textsuperscript{55} On the other hand, Sc\textsubscript{3}N@D\textsubscript{3}-C\textsubscript{68} contains 12 different types of carbons and 6 different types of C-C bonds (See Figure 1.4b). In this fullerene the addition of the malonate occurs on a bond exocylic to the pentalene patch that contains a unique [5,5]
bond only found in non-IPR fullerene cages.\textsuperscript{56} In Sc\textsubscript{3}N@\textit{D}_{3h}-C\textsubscript{68} scandium atoms are strongly coordinated to this pentalene patches.\textsuperscript{57}

Figure 1.5. Regioselectivity for multiple additions on Sc\textsubscript{3}N@\textit{D}_{3h}-C\textsubscript{78} (a) The three most preferred sites for the second addition of the adduct. (b) Projection of the LUMO onto the electron density surface of the Bingel-Hirsch monoadduct of Sc\textsubscript{3}N@\textit{D}_{3h}-C\textsubscript{78}. (Copyright ACS – See appendix A)

Further studies of the effect of the carbon cage on the reactivity of TNT-EMFs were made with the gadolinium series: Gd\textsubscript{3}N@\textit{I}_{h}-C\textsubscript{80}, \textit{C}_{3}(51365)-Gd\textsubscript{3}N@C\textsubscript{84}\textsuperscript{58} and Gd\textsubscript{3}N@C\textsubscript{88}.\textsuperscript{59} The Gd\textsubscript{3}N@\textit{I}_{h}-C\textsubscript{80} was found to be the most reactive whereas Gd\textsubscript{3}N@C\textsubscript{88} hardly reacted.\textsuperscript{59} These reactivity differences were explained based on the different pyramidalization angles on these fullerene cages. Recently it was found that diazoalkanes are very useful reagents for the functionalization of TNT-EMFs.\textsuperscript{60} By using this method the highly soluble phenyl-C\textsubscript{81}-butyric acid methyl esters (PCBMs) from M\textsubscript{3}N@\textit{I}_{h}-C\textsubscript{80} (M = Sc, Y) were obtained. This addition reaction occurs regioselectively on a [6,6] bond of the \textit{I}_{h}-C\textsubscript{80} fullerene cage as with the Bingel-Hirsch reactions.
1.3. Electrochemical Properties

Electrochemistry is a powerful technique for studying the electronic properties of fullerenes. The first electrochemical experiments on TNT-EMFs revealed that Sc$_3$N@$I_h$-C$_{80}$ has an electrochemical HOMO-LUMO gap of 1.86 V. This value is much smaller than that of C$_{60}$ (2.35 V), but, it is considerably higher than those of EMFs (typically under 1.0 V). The differences in the HOMO-LUMO gaps explain the higher abundance of TNT-EMFs compared to classical EMFs. The electrochemical redox potentials of TNT-EMFs with C$_{80}$ carbon cages are listed in Table 1.1. TNT-EMFs display electrochemically irreversible but chemically reversible reductive behavior. Except for TNT-EMFs containing the Sc$_3$N cluster, the LUMO orbital is mainly localized on the fullerene cage and the reductive electrochemical properties are strongly dependent on the symmetry of the carbon cage.

In the case of the TNT-EMFs containing the Sc$_3$N cluster, there is a significant participation of the trimetallic cluster on the LUMO. Experimental proof is provided by the electron paramagnetic resonance (EPR) spectrum of the Sc$_3$N@$I_h$-C$_{80}$ radical anion, which displays 22 hyperfine lines with a splitting constant of 55.6 Gauss, which is consistent with a high localization of the electronic spin on the Sc atoms (S=7/2). The EPR spectrum of the radical anion of Sc$_3$N@$D_5$-C$_{68}$ shows similar behavior, but it has much smaller hyperfine coupling constants (1.28 Gauss for the cation radical and 1.75 Gauss for the anion radical), suggesting that most of the unpaired spin is localized on the fullerene cage.
Table 1.1. Redox potentials of M$_3$N@C$_{80}$ in volts vs Fc/Fc$^+$ redox couple.

<table>
<thead>
<tr>
<th>TNT-EMF</th>
<th>$E^{+2}$</th>
<th>$E^{0/+}$</th>
<th>$E^{0/-}$</th>
<th>$E^{2/-2}$</th>
<th>$E^{2/-3}$</th>
<th>$\Delta(E^{0/+} - E^{0/-})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc$_3$N@I$<em>5$-C$</em>{80}$</td>
<td>-</td>
<td>+0.62</td>
<td>-1.24</td>
<td>-1.62</td>
<td>-</td>
<td>1.86</td>
</tr>
<tr>
<td>Sc$_3$N@I$<em>5$-C$</em>{80}$</td>
<td>+1.09</td>
<td>+0.59</td>
<td>-1.26</td>
<td>-1.62</td>
<td>-2.37</td>
<td>1.85</td>
</tr>
<tr>
<td>Sc$_3$N@I$<em>5$-C$</em>{80}$</td>
<td>-</td>
<td>+0.62</td>
<td>-1.22</td>
<td>-1.59</td>
<td>-1.90</td>
<td>1.84</td>
</tr>
<tr>
<td>Sc$_3$N@I$<em>5$-C$</em>{80}$</td>
<td>-</td>
<td>+0.59</td>
<td>-1.29</td>
<td>-1.56</td>
<td>-2.32</td>
<td>1.88</td>
</tr>
<tr>
<td>Sc$_3$N@I$<em>5$-C$</em>{80}$</td>
<td>-</td>
<td>+0.57</td>
<td>-1.27</td>
<td>-</td>
<td>-</td>
<td>1.84</td>
</tr>
<tr>
<td>Y$_3$N@I$<em>5$-C$</em>{80}$</td>
<td>-</td>
<td>+0.64</td>
<td>-1.44</td>
<td>-1.83</td>
<td>-2.38</td>
<td>2.08</td>
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<tr>
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<td>-</td>
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<tr>
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<td>+0.64</td>
<td>-1.42</td>
<td>-</td>
<td>-</td>
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<tr>
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<td>-1.31</td>
<td>-1.76</td>
<td>-</td>
<td>1.99</td>
</tr>
<tr>
<td>Tm$_3$N@I$<em>5$-C$</em>{80}$</td>
<td>-</td>
<td>+0.65</td>
<td>-1.43</td>
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<td>2.08</td>
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<tr>
<td>Er$_3$N@I$<em>5$-C$</em>{80}$</td>
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<td>+0.63</td>
<td>-1.42</td>
<td>-1.80</td>
<td>-</td>
<td>2.05</td>
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<tr>
<td>Dy$_3$N@I$<em>5$-C$</em>{80}$</td>
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<td>+0.70</td>
<td>-1.37</td>
<td>-1.86</td>
<td>-</td>
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<td>Gd$_3$N@I$<em>5$-C$</em>{80}$</td>
<td>-</td>
<td>+0.58</td>
<td>-1.44</td>
<td>-1.86</td>
<td>-2.18</td>
<td>2.02</td>
</tr>
<tr>
<td>Nd$_3$N@I$<em>5$-C$</em>{80}$</td>
<td>-</td>
<td>+0.63</td>
<td>-1.42</td>
<td>-</td>
<td>-</td>
<td>2.05</td>
</tr>
<tr>
<td>Pr$_3$N@I$<em>5$-C$</em>{80}$</td>
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<td>+0.59</td>
<td>-1.41</td>
<td>-</td>
<td>-</td>
<td>2.00</td>
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<tr>
<td>Sc$<em>3$N@D$</em>{5h}$-C$_{80}$</td>
<td>+0.70</td>
<td>+0.35</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sc$<em>3$N@D$</em>{5h}$-C$_{80}$</td>
<td>-</td>
<td>+0.34</td>
<td>-1.33</td>
<td>-</td>
<td>-</td>
<td>1.67</td>
</tr>
<tr>
<td>Lu$<em>3$N@D$</em>{5h}$-C$_{80}$</td>
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<td>+0.45</td>
<td>-1.41</td>
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<td>-</td>
<td>1.86</td>
</tr>
<tr>
<td>Dy$<em>3$N@D$</em>{5h}$-C$_{80}$</td>
<td>-</td>
<td>+0.41</td>
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<td>-1.85</td>
<td>-</td>
<td>1.81</td>
</tr>
<tr>
<td>Tm$<em>3$N@D$</em>{5h}$-C$_{80}$</td>
<td>-</td>
<td>+0.39</td>
<td>-1.45</td>
<td>-</td>
<td>-</td>
<td>1.84</td>
</tr>
</tbody>
</table>

On the anodic electrochemical scan there are no significant differences between TNT-EMFs with the same carbon cage and different encapsulated clusters. On the other hand, there are significant differences between TNT-EMFs with the same metal cluster but with
different carbon cages. Therefore, the fullerene cage orbitals have a strong participation in the HOMO orbital of the molecule.

Table 1.2. Redox potentials of M₃N@C₅₆ in volts vs Fc/Fc⁺ redox couple.

<table>
<thead>
<tr>
<th>TNT-EMF</th>
<th>E⁺⁺²</th>
<th>E⁰⁺</th>
<th>E⁰⁻</th>
<th>E⁻⁻²</th>
<th>E⁻⁻³</th>
<th>Δ(E⁰⁺ - E⁰⁻)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd₃N@C₈₀²⁺</td>
<td>-</td>
<td>+0.58</td>
<td>-1.44</td>
<td>-1.86</td>
<td>-2.18</td>
<td>2.02</td>
</tr>
<tr>
<td>Gd₃N@C₈₂²⁺</td>
<td>-</td>
<td>+0.37</td>
<td>-1.52</td>
<td>-1.86</td>
<td>-</td>
<td>1.89</td>
</tr>
<tr>
<td>Gd₃N@C₈₄²⁺</td>
<td>-</td>
<td>+0.32</td>
<td>-1.37</td>
<td>-1.76</td>
<td>-</td>
<td>1.69</td>
</tr>
<tr>
<td>Gd₃N@C₈₆²⁺</td>
<td>-</td>
<td>+0.35</td>
<td>-1.35</td>
<td>-1.70</td>
<td>-</td>
<td>1.70</td>
</tr>
<tr>
<td>Gd₃N@C₈₈²⁺</td>
<td>+0.49</td>
<td>+0.06</td>
<td>-1.43</td>
<td>-1.74</td>
<td>-</td>
<td>1.49</td>
</tr>
<tr>
<td>Nd₃N@C₈₀²⁺</td>
<td>-</td>
<td>+0.63</td>
<td>-1.42</td>
<td>-</td>
<td>-</td>
<td>2.05</td>
</tr>
<tr>
<td>Nd₃N@C₈₂²⁺</td>
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<td>+0.31</td>
<td>-1.44</td>
<td>-</td>
<td>-</td>
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<td>+0.07</td>
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<td>-</td>
<td>2.00</td>
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<tr>
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<tr>
<td>Pr₃N@C₈₈²⁺</td>
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<td>+0.09</td>
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<td>-</td>
<td>-</td>
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</tr>
<tr>
<td>Pr₃N@C₉₂²⁺</td>
<td>-</td>
<td>+0.35</td>
<td>-1.46</td>
<td>-</td>
<td>-</td>
<td>1.81</td>
</tr>
<tr>
<td>Pr₃N@C₉₆²⁺</td>
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<td>-1.54</td>
<td>-1.77</td>
<td>-</td>
<td>1.68</td>
</tr>
<tr>
<td>Ce₃N@C₈₈²⁺</td>
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<td>-</td>
<td>-</td>
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<tr>
<td>Ce₃N@C₉₂²⁺</td>
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<td>+0.32</td>
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<td>-</td>
<td>-</td>
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<td>Ce₃N@C₉₆²⁺</td>
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<td>+0.18</td>
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<td>-</td>
<td>1.68</td>
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<tr>
<td>La₃N@C₈₈²⁺</td>
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<td>+0.21</td>
<td>-1.36</td>
<td>-1.67</td>
<td>-</td>
<td>1.57</td>
</tr>
<tr>
<td>La₃N@C₉₂²⁺</td>
<td>-</td>
<td>+0.36</td>
<td>-1.44</td>
<td>-1.64</td>
<td>-</td>
<td>1.80</td>
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<tr>
<td>La₃N@C₉₆²⁺</td>
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<td>+0.14</td>
<td>-1.54</td>
<td>-1.77</td>
<td>-</td>
<td>1.68</td>
</tr>
<tr>
<td>Sc₃N@D₃h-C₆₈²⁺</td>
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<td>+0.33</td>
<td>-1.38</td>
<td>-1.98</td>
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</tr>
<tr>
<td>Sc₃N@D₃h-C₇₈²⁺</td>
<td>-</td>
<td>+0.12</td>
<td>-1.54</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Dy₃N@D₃h-C₇₈²⁺</td>
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<td>+0.47</td>
<td>-1.54</td>
<td>-1.93</td>
<td>-</td>
<td>2.01</td>
</tr>
</tbody>
</table>
The fact that TNT-EMFs are easier to oxidize than the ECFs is consistent with the presence of substantial charge transfer from the trimetallic cluster towards the fullerene cage. The differences of the oxidation potentials constitutes the basis of the chemical separation method that uses tris(4-bromophenyl)aminiumhexachloro antimonate, which selectively oxidizes the most reactive $D_{5h}$ isomer already mentioned.

The electrochemical properties of TNT-EMFs with the same cluster but with different carbon cages have been studied for the series of Gd$_3$N@C$_{2n}$, Nd$_3$N@C$_{2n}$, Pr$_3$N@C$_{2n}$, Ce$_3$N@C$_{2n}$ and La$_3$N@C$_{2n}$. The redox potentials in o-DCB vs Fc/Fc$^+$ are listed in Table 1.2. There are big differences in the first oxidation potential within the same trimetallic nitride cluster series, confirming that the HOMO orbital is localized mainly on the fullerene cage. On the other hand, the variation of the first reduction potential correlates with the electronegativity of the metal.

![Figure 1.6. Reductive electrochemical behavior of TNT-EMF derivatives.](image)
The electrochemical properties of the TNT-EMFs can be modulated by chemical functionalization. It was found that the \(N\)-ethyl-[5,6]-pyrrolidine derivatives of the \(M_3N@I_h-C_{80}\) (\(M = \text{Sc, Y and Er}\)) have reversible reductive electrochemical behavior whereas the \(N\)-ethyl-[6,6]-pyrrolidine derivatives of \(M_3N@I_h-C_{80}\) (\(M = \text{Y and Er}\)) have irreversible behavior, as observed for the pristine TNT-EMFs.\(^{28}\) The [6,6] TNT-EMF “fulleroids” from the Bingel-Hirsch reaction, the PCBM derivatives obtained by the reaction with diazoalkanes\(^{60}\) and the 1,4 free radical addition products\(^{45,46}\) all exhibit irreversible reductive electrochemical behavior as for the pristine cages as well.\(^{28}\) The reductive electrochemical behavior of TNT-EMF derivatives is illustrated in Figure 1.6. Pyrrolidine derivatives display two oxidation processes corresponding to the oxidation of the fullerene cage and an extra irreversible oxidation process that corresponds to oxidation of pyrrolidine which leads to the retro 1,3-dipolar cycloaddition reaction.\(^{43}\) All the other derivatives reported so far are stable under oxidative conditions.
2. Organic Solar Cells

2.1. Discovery and evolution

The photovoltaic effect with organic compounds was observed in the late 50s. At that time organic solar cells were fabricated by sandwiching a crystal or a crystalline thin film of an organic compound between two electrodes with different working functions trying to mimic a classical pn-junction as in silicon solar cells. In spite of these promising results, the overall efficiencies of these devices were extremely low (~1.0 * 10^-4 %). In the 80’s a bilayer solar cell was built using copper phthalocyanine as the p-type material and perylenetetracarboxylic acid diimide as n-type. This cell reached 1% efficiency, which was considered a milestone in organic photovoltaics at the time.

In the early 90’s two groups reported independently the introduction of C_60 as dopand together with conductive polymers, poly((2-methoxy-5-(2’-ethylhexoxy)-p-phenylene)vinylene (MEH-PPV) and poly(3-hexylhexathiophene) (P3HT). In the presence of light, electron transfer from the excited state of the polymer towards the fullerene occurs, creating free charges in the bulk that considerably increase the conductance of these polymers, thus this process is usually referred to as photo-doping. These observations led to the development of a photodiode based on a C_60 doped MEH-PPV junction with a rectification ratio ~ 10^4 and its possible application as a photo-detector or solar cell was suggested. Bilayer devices using semiconductor polymers as donors and fullerenes as acceptors were built, but the overall efficiencies obtained were under 0.1%. 
Contrary to what happens in silicon solar cells where the photons induce the direct formation of charges; in organic solar cells once a photon is absorbed, it creates a neutral mobile excited state called an “exciton”. Excitons are dissociated into free charges at the interface between the \( p \)-type(donor) and \( n \)-type(acceptor) materials or at the interfaces between the organic materials and the electrodes. The generated charges migrate towards the electrodes because of the built-in electrical field produced by the different work functions of the electrodes, creating a photocurrent (See Figure 1.7). The average diffusion distance of the excitons is very low (typically 5-15 nm) and since they are neutral, they are not affected by the electric field. Most of the formed excitons in the bulk decay to the ground state before reaching a material interface or one of the electrodes, leading to efficiency losses. Therefore, the desirable layer size should be equal to or be no larger than twice the average exciton diffusion distance, but thick enough to allow the absorption of most of the incoming light and the conduction of the free charges to the

![Figure 1.7. Working principle of organic solar cells.](image)
respective electrodes. These requirements were first met in the bulk hetero junction solar cell.\textsuperscript{90}

2.2. Bulk hetero junction concept

A significant increase of the efficiency of the organic solar cells built using MEH-PPV doped with 1-(3-methoxycarbonyl)propyl-1-phenyl-[6,6]-C\textsubscript{61} (PCBM) was made when the planar devices were replaced with a phase separated composite used as the active layer (See Figure 1.8).\textsuperscript{90} This interpenetrating network of donor and acceptor materials or “Bulk Hetero Junction” (BHJ) allows a more efficient charge separation because it increases the D-A contact area where the excitons created in the bulk by the incoming light can be separated into free charges.

![Top transparent electrode (usually indium tin oxide (ITO) - anode](image1)

![Bottom electrode (usually aluminum) - cathode](image2)

Figure 1.8. Organic solar cell assemblies (a) bilayer solar cell (b) Bulk heterojunction solar cell. In both cases the donor material is represented in blue color and the acceptor in white.

The bulk heterojunction organic solar cells (BHJOSCs) are the current dominating technology in the field of organic solar cells\textsuperscript{91} and they are made as follows. In the first step of fabrication, a solution containing the polymer and the fullerene derivative in a \(\sim 1:3\) ratio is used to print a thin layer (\(\sim 80\) nm) of active material on top of an ITO
electrode covered with a 50 nm electron blocking thin film layer of poly(3,4-ethylenedioxylenethiophene)-polystyrene sulfonic acid (PEDOT:PSS). Once the solvent has been evaporated and the two phases have been separated; the active layer is covered with LiF, which acts as a hole blocking layer and finally the cathode is built by high vacuum deposition of either aluminum or silver metal.

Figure 1.9. Materials used in the fabrication of highly efficient organic solar cells. (P7BT - donor material, PC71BM - acceptor material)

Most of the BHJOSCs are subject to a post-fabrication annealing treatment to further improve the phase donor-acceptor separation. This approach is used to fabricate the most efficient organic solar cell known today, which has reached a value of 7.4%. However, “Solarmer” an organic solar cells company, claims to have reached an efficiency value of 8.13% as for 10-01-2010.

2.3. Molecular junctions

Despite the remarkable efficiencies obtained so far the overall efficiency of organic solar cells is extremely dependent on the materials used and the fabrication process. In
fact, several authors have reported different efficiencies for devices fabricated under the same conditions but using donor polymers from diverse commercial sources\textsuperscript{91} because of differences in purity and stereo regularity of the polymers. Another major drawback is that the phases have a tendency to separate from each other after prolonged exposure to solar radiation, because of the high temperatures that considerably decrease the contact area between the donor and acceptor phases that not only decrease the overall power efficiency\textsuperscript{97} but also the lifespan of the cells. There are diverse alternatives to overcome these problems such as molecular bulk heterojunctions built with small molecule donors,\textsuperscript{98,99} single molecule donor-acceptor systems (See Figure 1.10) also known as molecular heterojunctions,\textsuperscript{100-103} self assembling systems,\textsuperscript{104-106} or monomers containing both the donor and the acceptor moieties that after polymerization produce the desired donor and acceptor phases, also known as “double cable polymers”.\textsuperscript{107} The basic ideas behind all these approaches is to tune the properties at the molecular level.\textsuperscript{108-110}

![Figure 1.10. Example of single molecule donor-acceptor system.\textsuperscript{101}](image)

The processes occurring in an organic solar cell are similar to the processes occurring in a natural photo-synthetic system\textsuperscript{108,111} and every part of these molecular junctions
Fullerenes play an important role in the process of charge separation. Fullerenes are not only used as electron acceptor materials in the construction of bulk heterojunction systems described before, but also in the preparation of single molecule donor acceptor systems because of their unique electronic properties. Due to the high surface conjugation on the surface they can easily delocalize electrons and they have very low energy LUMOs. In the case of C$_{60}$ the LUMO is triply degenerate so it can accept up to six electrons. However, the most important parameters that make fullerenes unique is that they have low reorganization energies upon reduction; that is the geometry of the molecule is barely distorted after multiple reductions and 3D structures that favors the multidimensional conduction. According to Marcus’ theory of electron transfer, two factors dominate electron transfer processes: the electronic coupling between the donor and the acceptor and the reorganization energy. Low reorganization energy favors charge separation while slowing down the charge recombination leading to long lived charge separated states.

Figure 1.11. Typical molecules used as donors in the construction of donor-acceptor systems. (a) Ferrocene (b) Tetrathiafulvalene (TTF) (c) Phthalocyanine (d) Porphyrin

The choice for donor molecules is broader (See Figure 1.11). Porphyrins are a “natural” choice due to the presence of porphyrin rings in the natural photosynthetic
systems.\textsuperscript{117} They are also popular because of their high chemical stability, ease of preparation\textsuperscript{118} and high absorption in the visible range. Phthalocyanines are also popular because their absorption spectra have a better match with the solar emission spectrum in fact, they have extinction coefficients as high as 200,000 M\textsuperscript{-1}cm\textsuperscript{-1} in the 700 nm wavelength range, which can lead to enhanced solar energy conversion.\textsuperscript{119}

The nature of the bridge between the donor and the acceptor is also important. This is in fact what makes the whole electron transfer process in molecular junctions both tunable and predictable.\textsuperscript{120} Since the rates of electron transfer and charge recombination are mainly controlled by electronic coupling and reorganization energy, the geometry and the electronic properties of the bridge can have a large impact on the charge separation process. The orbitals of the bridge can participate in both charge separation and charge recombination processes.\textsuperscript{121} On the other hand, the preferred conformation of the donor-acceptor system determines whether through space or through bond interactions are favored.
3. Aim of the thesis

The main purpose of this work is the synthesis of TNT-EMFs derivatives and the study of their electrochemical properties in order to evaluate their potential application in the fabrication of molecular hetero-junction organic solar cells. Evaluation of the intramolecular charge transfer properties was made by our collaborator Professor Dirk Guldi at Friedrich-Alexander Universität Erlangen-Nürnberg in Germany.

In Chapter 2 the synthesis of D-A systems based on TNT-EMFs comprising different metals and different donor systems is presented. Some inherent problems arising from the nature of the TNT-EMF family are described, as well as the characterization of the compounds and the most relevant results resulting from the theoretical and photophysical studies made by our collaborators that show how the derivatives are capable of producing longer lived charge separated states in solution than their C_{60} analogous compounds.

In Chapter 3 the synthesis of D-A systems designed for optimal charge separation processes in D-A systems is described. The topology and the length of the linker were varied for different systems and the electrochemical characterization and photophysical results obtained by our collaborators are presented.

In Chapter 4 the synthesis and electrochemical studies of TNT-EMFs with Bingel-Hirsch adducts are described. We found appropriate conditions to prepare these derivatives with Sc_{3}N@I_{h}-C_{80} and Lu_{3}N@I_{h}-C_{80}, which are the most abundant TNT-EMFs known and we studied the influence of the functionalization on the reductive electrochemical behavior of the derivatives. This is especially relevant for Lu_{3}N@I_{h}-C_{80} because of its high reduction potential which makes it one of the most promising
fullerenes to be used as acceptors in organic solar cells. Its high energy LUMO orbital helps to minimize the energy loss during the charge separation process and to increase the open circuit voltage. Both of these effects contribute to a higher overall efficiency of the resulting solar device. TGA studies of some of these derivatives were made and compared to reference compounds in order to evaluate their capacity to withstand the harsh temperature conditions found in solar cell devices.

In Chapter 5 the preparation of electro-active films by electrooxidative-polymerization of triphenylamine-TNT-EMF derivatives is presented. The main goal was to find a practical way to incorporate TNT-EMF based D-A systems with inherently low solubility in the construction of solar cell devices while trying to improve the conductance properties of the organic solar cells.

Finally in Chapter 6 the optimization for the preparation of Sc₂S@C₂ₙ (n = 40–50), a new family of high yield endohedral metallofullerenes, is presented. Different arcing conditions were tested in order to evaluate the effect of rod preparation, current, voltage gap and atmosphere conditions on the yield of these fullerenes. The electrochemical studies were made and compared to TNT-EMFs and the recently discovered metal oxide endohedral fullerene family.
1. Introduction

Single molecule donor – acceptor (D-A) systems are molecules in which an electron transfer reaction can occur between two different parts or atoms in a molecule. The rates of electron transfer reactions can vary considerably even though the process involves only a short displacement of one electron.\cite{123,124} Despite bonds are neither broken nor formed during the electron transfer reaction, the equilibrium position of the atoms and the position of the solvent molecules solvating the dyad change due to dipolar interactions and the energy required for those changes to occur is called the reorganization energy ($\lambda$).

In figure 2.1 $E_a$ represents the activation energy that according to Marcus’ theory of electron transfer,\cite{113-115} it can be described in terms of the reorganization energy ($\lambda$) and the free energy of the reaction ($\Delta G^0$) as follows:

$$E_a = \left(\frac{\Delta G^0 + \lambda}{4\lambda}\right)^2$$  \hspace{1cm} (Equation 1)

Arrhenius equation (equation 2) shows the dependence of the reaction rate with the activation energy ($E_a$), so by plugging equation 1 and 2 it is shown that the reaction rates of electron transfer reactions depend on the free energy ($\Delta G^0$) and the reorganization energy ($\lambda$).

$$k = Ae^{\left(\frac{E_a}{RT}\right)}$$  \hspace{1cm} (Equation 2)

$$\therefore k = Ae^{\left(\frac{\left(\Delta G^0 + \lambda\right)^2}{4\lambda RT}\right)}$$  \hspace{1cm} (Equation 3)
Figure 2.1 Diabatic potential energy surfaces for electron transfer reactions. (a) if $\Delta G = 0$ then $E_a = \lambda/4$ (b) if the reorganization energy has the same value as the $\Delta G^0$ of the reaction $E_a$ becomes 0 and the reaction occurs at the highest possible rate (c) when the $\Delta G^0 > \lambda$ the inverted region is reached and $E_a$ starts increasing as $\Delta G^0$ of the reaction increases slowing down the rate of the reaction (See equation 3).

The quadratic dependence of the reaction rate on $\Delta G^0$ explains the great variation observed experimentally for different reactions and the inverted region has important consequences on the design of donor acceptor systems because making fall the charge recombination reaction (which liberates a high amount of energy) into the inverted region of the Marcus parabola is highly desired because it slow down its rate hence favoring the charge separation.

The design of single molecule donor – acceptor systems is of interest because photosynthesis has its roots in an electron transfer process. Artificial systems capable of successfully mimicking photosynthesis can be used to capture energy from diverse light sources and use the harvested energy for either driving redox chemical reactions or for the direct construction of light sensitive electronic devices such as photo-sensors or solar cells. Based on their electronic properties, the use of fullerenes for the construction of donor acceptor systems was initiated some time ago and the
preparation of highly effective systems capable of producing charge separated states with lifetimes longer than those observed in nature have been realized.\textsuperscript{108}

Until now the construction of donor – acceptor systems using fullerenes as the acceptor moiety has been dominated by the use of \textit{C}_{60}. However, the interesting properties displayed by TNT-EMFs make them attractive to substitute \textit{C}_{60} in this application. The early studies of the electrochemical properties of TNT-EMFs revealed that they have smaller HOMO-LUMO gaps\textsuperscript{19} and consequently higher light absorption that extends towards the visible range of the spectrum. Theoretical calculations have established that the LUMO orbital in Sc\textsubscript{3}N@Ir-C\textsubscript{80} has a strong contribution from the metal cluster.\textsuperscript{130} Therefore the encapsulated cluster may have a strong influence on the charge separation process. The different electrochemical behavior observed depending upon the functionalization position\textsuperscript{28} further opens the possibility to either control or modulate the behavior of the resulting dyads. Here we describe the preparation of covalently linked donor – acceptor systems using some common electron donors and TNT-EMFs as the electron acceptors.

Part of the experimental procedures and graphs presented here are a pre-peer reviewed version of the following articles (See Appendix B for the copyright letter):


2. Synthesis of the compounds

Two different strategies were used for the preparation of TNT-EMF dyads based on the differences on the reactivity depending on the encapsulated cluster.\textsuperscript{27,28} Due to the limited amount of TNT-EMFs available, only 2-ferrocenyl-[5,6]-Sc\textsubscript{3}N@I\textsubscript{η}-C\textsubscript{80} was prepared in a larger scale and sent to our collaborators for photochemical studies. Sc\textsubscript{3}N@I\textsubscript{η}-C\textsubscript{80} was purified from a crude mixture of Sc\textsubscript{3}N@C\textsubscript{2n} (n=34, 39, 40) provided by Luna Innovations Inc. using tris(4-bromophenyl)aminium hexachloroantimonate (magic blue) and a modification of the originally reported method.\textsuperscript{20} Y\textsubscript{3}N@C\textsubscript{80} was used without further purification due to the low content and higher reactivity of the $D_{5h}$ isomer and Lu\textsubscript{3}N@I\textsubscript{η}-C\textsubscript{80} was prepared and separated from the crude fullerenes extract by two HPLC stages using first a pentabromobenzyl functionalized silica PBB (4.6 x 250 mm) followed by a 3-(1-pyrenyl)propyl functionalized silica Buckyprep (10 x 250 mm) column eluting with toluene.\textsuperscript{131}

2.1. Ferrocene based dyads

Ferrocene is commonly used for the construction of covalently linked donor acceptor systems because the ferrocenyl centers can be reversible oxidized.\textsuperscript{132,133} Although the direct application of ferrocene based donor acceptor systems in the construction of solar cell devices is very limited, it constitutes a good testing system. For that reason we started by preparing donor acceptor systems with M\textsubscript{3}N@I\textsubscript{η}-C\textsubscript{80} (M=Sc, Y) using the 1,3-dipolar cycloaddition reaction (Prato reaction).\textsuperscript{32,33} The differential reactivity between
Sc$_3$N@$I_h$-C$_{80}$ and Y$_3$N@$I_h$-C$_{80}$ allowed us to obtain a [5,6] in the case Sc$_3$N@$I_h$-C$_{80}$ and a [6,6] fulleropyrrolidine dyad in the case of Y$_3$N@$I_h$-C$_{80}$.

2.1.1. Purification of Sc$_3$N@$I_h$-C$_{80}$

The original reported procedure was modified to reduce the time of contact between the fullerene mixture and the oxidant agent; in order to obtain higher and reproducible yields. The modification consisted of packing a chromatography column (2.5 cm internal diameter – 25.0 cm long) with flash chromatography silica gel (Sorbent 60 Å 230–400 mesh) suspended in CS$_2$. The suspension is loaded into the column and compacted using nitrogen pressure (<5 psi) in batches until the level of compacted silica inside the column is about ~15 cm high (Caution CS$_2$ is an extremely flammable solvent. The whole process has to be done under a hood far away from heat or spark sources).

Figure 2.2 Purification of Sc$_3$N@$I_h$-C$_{80}$ by selective oxidation. (a) The “magic blue” is layered in the silica gel. The starting fullerene solution mixture is poured at the top. (b) The fullerene mixture once it starts eluting (c) The first fraction after crossing the magic blue layer (d) The appearance of the column once the Sc$_3$N@$I_h$-C$_{80}$ fraction has been collected.
A suspension of 20 mg of “magic blue” in CS$_2$ was loaded into the column carefully in order not to disturb the surface of the silica gel. Then the solvent was flowed until there was no solvent above the silica and a thin layer of “magic blue” was formed; additional solvent may be used to rinse the internal wall of the column and to ensure that all the oxidant forms a thin layer on top of the silica. Once the “magic blue” layer is dry, silica gel is carefully added on top of the magic blue without breaking the thin oxidant layer until a five centimeters layer of silica is created. 5.0 mL of a filtered saturated solution of Sc$_3$N@C$_{2n}$ (n=34, 39, 40) in CS$_2$ (fullerene mass ~5.0 mg) was poured at the top of the column and eluted by gravity using CS$_2$ (See Figure 2.2). The fraction eluting with the solvent front was collected, the solvent evaporated and the remaining solid washed with diethyl ether and/or dichloromethane to remove the tris(4-bromophenyl)amine (visible under UV-light) and the monoadduct formed by the replacement of a bromine atom of this amine by Sc$_3$N@C$_{80}$.

Figure 2.3 Purification of Sc$_3$N@I$_{n}$-C$_{80}$ followed by MALDI-TOF mass spectrometry. (a) Crude Sc$_3$N@C$_{2n}$ (n=34, 39, 40) fullerene mixture (b) Fullerene fraction collected after the reaction with “Magic blue”. The peak at 1508.8 corresponds to MB-Sc$_3$N@I$_{n}$-C$_{80}$ monoadduct (c) Pure Sc$_3$N@I$_{n}$-C$_{80}$. 

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The Sc$_3$N@$I_h$-C$_{80}$ powder was recovered from the ethyl ether/dichloromethane suspension by filtration using a Teflon syringe HPLC (0.2 µm pore size) filter. The syringe can be used for further solvent washing. Sc$_3$N@$I_h$-C$_{80}$ was recovered from the filter with a solvent mixture of CS$_2$/o-DCB 4:1. Finally the resulting solution was dried in a 20 mL vial under a slow stream of nitrogen overnight to yield crystalline Sc$_3$N@$I_h$-C$_{80}$. Typically 2.0 to 2.2 mg of crystalline Sc$_3$N@$I_h$-C$_{80}$ are obtained starting from 5.0 mg of Sc$_3$N@C$_{2n}$ (n=34, 39, 40) mixture when using this purification method. The purification process was followed by Matrix Assisted Laser Desorption/Ionization (MALDI) spectroscopy (See Figure 2.3) and Osteryoung Square Wave Voltammetry (OSWV) (See Figure 2.4). The electrochemical method is the best option because the Sc$_3$N@$I_h$-C$_{80}$ and Sc$_3$N@$D_{5h}$-C$_{80}$ have very close retention times in the HPLC columns and not all the fullerenes exhibit similar volatility in the mass spectrometer.

![Figure 2.4 Purification of Sc$_3$N@$I_h$-C$_{80}$ followed by Osteryoung Square Wave Voltammetry (OSWV). (a) Sc$_3$N@$I_h$-C$_{80}$ trace (b) starting mixture. Tetrabutylammonium hexafluorophosphate 0.05 M in o-DCB was used as the supporting electrolyte and the potentials were calibrated vs Fe/Fe$^+$ redox pair.](image)
2.1.2. Synthesis of N-Methyl-2-ferrocenyl-[5,6]-Sc₃N@I₆-C₈₀-fulleropyrrolidine

![Figure 2.5 Synthesis of N-Methyl-2-ferrocenyl-[5,6]-Sc₃N@I₆-C₈₀-fulleropyrrolidine.](image)

In a Schlenk flask equipped with a magnetic stirring bar under argon were charged 2.21 mg of Sc₃N@I₆-C₈₀ (2.0 µmol, 1 equiv), 2.80 mg of N-methylglycine (31.0 µmol, 15 equiv) and 20.78 mg of ferrocene carboxaldehyde (97.0 µmol, 49 equiv). These materials were dissolved in 20 mL of a solvent mixture of anhydrous toluene and anhydrous o-DCB in a 1:1 ratio and heated up for 45 minutes at 120 °C while stirring. The reaction was followed by using TLC silica plates eluting with a solvent mixture of CS₂ and toluene in a 2:1 ratio. Once the formation of bis- and poly-adducts was evident on the TLC plates the reaction mixture was removed from the heating bath to stop the reaction and the solvent evaporated using a stream of nitrogen under the hood until the total volume was ~5.0 mL. This reaction mixture was purified using flash chromatography charging the column and eluting first with pure CS₂ to recover the un-reacted Sc₃N@I₆-C₈₀ followed by a 1:1 CS₂/Toluene solvent mixture to recover the product. The solvent was evaporated to dryness and the solid washed with diethyl ether to remove the grease impurities from CS₂ and dried under vacuum to remove the diethyl ether before the
analysis. 1.20 mg of product was obtained (44 % yield based on Sc$_3$N@I$_h$-C$_{80}$). $^1$H NMR (500 MHz, CS$_2$/o-DCB-d$_4$ 3:2, referenced to the residual solvent signal): $\delta$ 4.70 (br, 1H), 4.53 (br, 1H), 4.39 (br, 1H), 4.27 (br, 1H), 4.25 (s, 5H; Cp), 4.21 (d, 1H, $^2$$J_{(H,H)}$=9.5 Hz), 3.65 (s, 1 H), 3.01 (d, 1H, $^2$$J_{(H,H)}$=9.5 Hz), 3.20 ppm (s, 3H; CH$_3$). The purity of the compound was evaluated by HPLC using a Buckyclutcher (10 x 250 mm) column eluting with toluene at a flow rate of 4.0 mL/min (See Figure 2.6). Compound 1 has a retention time of 11.3 min under these conditions.

The 500 MHz $^1$H NMR spectrum of 1, recorded in a solvent mixture of CS$_2$/o-DCB-d$_4$ 3:2, shows the resonances for the protons in the Cp ring connected to the pyrrolidine as broad signals at 4.70, 4.53, 4.39 and 4.27 ppm and the resonance for the 5 protons in the other Cp ring as a sharp singlet at 4.25 ppm. The protons of the methylene group in the pyrrolidine ring are diastereotopic and appear as two doubles at 4.21 and 3.01 ppm respectively; they have a germinal coupling constant of 9.5 Hz. The resonance of the
proton in the pyrrolidine ring connected to the carbon that holds the ferrocenyl group is observed as a singlet at 3.65 ppm and the methyl group connected to the nitrogen as a sharp singlet at 3.20 ppm.

Figure 2.7 $^1$H-$^1$H-COSY spectrum of $N$-Methyl-2-ferrocenyl-[5,6]-Sc$_3$N@$I_8$-C$_{80}$ fulleropyrrolidine

The correlations among the protons in the substituted Cp ring and between the protons in the pyrrolidine ring are clearly observed in the $^1$H-$^1$H-COSY spectrum (See Figure 2.7). The $^1$H-$^{13}$C HMQC spectrum (See Figure 2.8) of 1 shows the correlation of the doublet signals at 4.21 and 3.01 from the diastereotopic protons with a carbon around
72 ppm and the correlation of the signal at 3.65 with a carbon around 80 ppm. These correlations are in good agreement with the chemical shift for the carbons directly attached to the fullerene cage in the $N$-ethyl-$[5,6]$-Sc$_3$N@$I_h$-C$_{80}$ fulleropyrrolidine\textsuperscript{32} which are observed at 70.09 ppm and the downfield displacement of the two signals can be attributed to the deshielding effect of the ferrocenyl substituent.

Figure 2.8 $^1$H-$^1$C-HMQC spectrum of $N$-Methyl-2-ferroceny-$[5,6]$-Sc$_3$N@$I_h$-C$_{80}$ fulleropyrrolidine

The methyl group carbon has a resonance $\sim$40 ppm and the carbons in the Cp rings are observed between 65 and 70 ppm.
Finally the MALDI mass spectrum of 1 was recorded using 9-nitroanthracene as matrix and negative ionization mode (See Figure 2.9). The molecular peak of 1 is observed (m/z: 1350.15) along with a fragmentation peak corresponding to Sc$_3$N@I$_{h}$-C$_{80}$ (m/z: 1109.73). The observed isotopic pattern is in good agreement with the calculated one.

2.1.3. Synthesis of N-Methyl-2-ferrocenyl-[6,6]-Y$_3$N@I$_{h}$-C$_{80}$-fulleropyrrolidine

![Synthesis of N-Methyl-2-ferrocenyl-[6,6]-Y$_3$N@I$_{h}$-C$_{80}$-fulleropyrrolidine](image)
Using a similar procedure to that used to prepare 1, 1.17 mg of Y$_3$N@I$_h$-C$_{80}$ (0.94 µmol, 1 equiv), 1.32 mg of N-methylglycine (14.9 µmol, 15.8 equiv) and 10.4 mg of ferrocene carboxaldehyde (48 µmol, 51.7 equiv) were charged into a Schlenk flask under argon. Then 10 mL of anhydrous o-DCB were added using a syringe. The mixture was heated and stirred magnetically for 2 h at 120 °C using a preheated oil bath and the progress of the reaction was followed by TLC using silica plates eluting with a solvent mixture of CS$_2$/toluene mixed in a 2:1 ratio. The solvent was evaporated under a stream of nitrogen to dryness. The reaction mixture was purified using preparative TLC plates (Sorbent 60Å pore, particle size 5 – 17 µm, 500 µm thick) first with CS$_2$ in order to recover the unreacted Y$_3$N@I$_h$-C$_{80}$ which eluted with the solvent front.

Figure 2.11 Purification of N-Methyl-2-ferrocenyl-[6,6]-Y$_3$N@I$_h$-C$_{80}$-fulleropyrrolidine. The unreacted Y$_3$N@I$_h$-C$_{80}$ elutes with the solvent front and the product elutes as a black band Rf=0.85 with a 3:2 solvent mixture of CS$_2$/toluene.
The plate was dried and eluted again with a 3:2 mixture of CS₂ and toluene to elute the desired product, which elutes as a black band (Rf = 0.85). The product was recovered from the silica using CS₂ and the resulting solution evaporated to dryness. Then the residual solid was washed with diethyl ether to remove the grease contaminants from CS₂ to obtain 0.63 mg of a black powder (45.2% yield based on Y₃N@I₇-C₈₀). ¹H NMR (500 MHz, CS₂/acetone-d₆ 9:1, 25°C, TMS): δ 4.55 (br, 1H), 4.46 (br, 1H) 4.35 (br, 1H), 4.31 (br, 1H), 4.20 (s, 5H; Cp), 4.20 (d, 1H, ¹J(ν,ν)=9.5 Hz), 3.63 (s, 1H), 2.99 (d, 1H, ¹J(ν,ν)=9.5 Hz), 3.14 ppm (s, 3H; CH₃).

Figure 2.12 HPLC trace of N-Methyl-2-ferrocenyl-[6,6]-Y₃N@I₇-C₈₀ fulleropyrrolidine. (a) Starting Y₃N@I₇-C₈₀ (b) N-Methyl-2-ferrocenyl-[6,6]-Y₃N@I₇-C₈₀ fulleropyrrolidine. HPLC conditions Buckyclutcher column (10 x 250mm) / toluene 4.0 mL/min.

The purity of the compound was evaluated by HPLC using a Buckyclutcher (10 x 250 mm) column eluting with toluene at a flow rate of 4.0 mL/min (See Figure 2.12). Compound 2 has a retention time of 9.3 min under these conditions. The difference in retention time compared to compound 1 is due to the different substitution pattern on the I₇-C₈₀ cage which modifies the interactions between the derivative and the stationary
phase in the column. This behavior has been observed previously for [5,6] and [6,6] fulleropyrrolidine derivatives of TNT-EMFs.\textsuperscript{28,35,37,38}

Figure 2.13. 500 MHz \textsuperscript{1}H NMR spectrum of N-Methyl-2-ferrocenyl-[6,6]-Y\textsubscript{3}N@I\textsubscript{r}-C\textsubscript{80}-fulleropyrrolidine. * Impurities from the solvent.

The \textsuperscript{1}H NMR spectrum of compound 2 is similar to that of compound 1 (See Figure 2.13). However, due to symmetry considerations the addition of a non-symmetric azomethine ylide to the surface of the I\textsubscript{r}-C\textsubscript{80} cage on a [6,6] bond should produce a mixture of two pairs of enantiomers (See Figure 2.14), but only a set of signals is
observed indicating that only one pair of enantiomers is present in the isolated fraction. Therefore, it can be inferred that there is a preference in the regioselectivity of the addition. This is not surprising because there are many examples where additions of azomethine ylides over asymmetric olefin substrates which are strongly influenced by steric and electronic factors.\textsuperscript{134-136}

Figure 2.14 [5,6] vs [6,6] addition pattern of non-symmetric azomethine ylides on the $I_h$-C\textsubscript{80} cage. (a) The [5,6] addition pattern produces only one pair of enantiomers. (b) The [6,6] addition pattern produces two pairs of enantiomers.

The resonances for the protons in the Cp ring directly connected to the pyrrolidine ring are observed at 4.55, 4.46, 4.35 and 4.31 ppm. The 5 protons in the other Cp ring show a sharp singlet at 4.20 ppm; the diastereotopic protons in the pyrrolidine ring are observed as doublets with a geminal coupling constant of 9.5 Hz at 4.20 and 2.99 ppm, respectively. Finally the protons in the $N$-methyl group are observed as a singlet at 3.14 ppm. The MALDI-TOF spectrum of compound 2 only showed only a peak corresponding to $Y_3N@I_h$-C\textsubscript{80} ($m/z$: 1241.7).
The isomerization of compound 2 into the [5,6] isomer was attempted by heating an o-DCB solution of 2 at 150°C, but instead of the isomerization process previously observed for similar systems, the 1,3-retrocycloaddition reaction occurred to yield Y₃N@I₇-C₈₀ as the only product. This decomposition process was observed at room temperature as well. When compound 2 was left in solution it decomposed into Y₃N@I₇-C₈₀ after a few days.

2.2. exTTF based dyads

Tetrathiofulvalene (TTF) is well known because it forms a charge transfer complex when it is mixed in a 1:1 ratio with the electron acceptor tetracyano-p-quinodimethane (TCNQ). This charge transfer complex behaves as a metal in a wide range of temperatures and it has a very high electrical conductivity (1.47 x 10⁴ ohm⁻¹ cm⁻¹ at 66 °K) . 2-[9-(1,3-dithiol-2-ylidene)anthracen-10(9H)-ylidene]-1,3-dithiole (exTTF) is a donor molecule sharing characteristics with TTF and has been successfully applied to the construction of C₆₀ donor acceptor systems.¹¹⁰,¹³⁸

![Figure 2.15 Geometry changes of exTTF after redox reactions. Left – ground state, right – oxidized state.](image)
Contrary to other donor systems, exTTF is a ground state donor system and the driving force for this process to occur is that exTTF undergoes aromatization after oxidation at relatively low potentials yielding thermodynamically stable mono cationic or di-cationic species where the dithiolium cation rings are orthogonal to the anthracene core\(^{138}\). (See Figure 2.15). These conformational changes may impact the reorganization energies hence the lifetime of the charge separated states of the donor – acceptor systems built with exTTF. However, the main reason for using exTTF or generally TTF systems is because of the enhanced conductance properties.

2.2.1. Synthesis of 81-[9,10-Bis(1,3-dithiol-2-ylidene)-9,10-dihydro-2-anthracenylmethyloxycarbonyl]-81-(ethoxycarbonyl)-1,2-methano-[6,6]-Y\(_3\)N@I\(_h\)-C\(_{80}\)] fullerene

![Synthesis of 81-[9,10-Bis(1,3-dithiol-2-ylidene)-9,10-dihydro-2-anthracenylmethyloxycarbonyl]-81-(ethoxycarbonyl)-1,2-methano-[6,6]-Y\(_3\)N@I\(_h\)-C\(_{80}\)] fullerene

Figure 2.16 Synthesis of 81-[9,10-Bis(1,3-dithiol-2-ylidene)-9,10-dihydro-2-anthracenylmethyloxycarbonyl]-81-(ethoxycarbonyl)-1,2-methano-[6,6]-Y\(_3\)N@I\(_h\)-C\(_{80}\)] fullerene

9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydro-2-anthracenylhydroxymethyl-2-bromoethyl malonate 3 was prepared according to the procedure reported in the literature\(^{139}\) in a three step process starting from 2-formyl-9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (exTTF-CHO) provided by Professor’s Nazario Martin group. 40.1 mg of compound 3 (66.3 µmol, 3.4 equiv) and 11.8 mg of Y\(_3\)N@C\(_{80}\) (9.5 µmol, 1 equiv)
was placed in a round bottomed flask equipped with a magnetic stirring bar. The system was dried under vacuum and then filled with argon. 10 mL of o-DCB were added and agitation started; then 10.0 µL of 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (66.0 µmol) dissolved in 1.0 mL of CHCl₃ was added dropwise. The progress of the reaction was followed by TLC using silica gel plates and eluting first with CS₂ to elute the un-reacted Y₃N@I₆-C₈₀. After drying the plates, they were eluted with CHCl₃. The product elutes almost with the solvent front. When a second fraction began to appear, the reaction was stopped. The reaction mixture was then concentrated under vacuum and purified on preparative TLC silica plates. The product was recovered from the silica using CHCl₃ and dried to obtain 1.6 mg of the title compound (13.5% yield based on reacted Y₃N@I₆-C₈₀).

The purity of compound 4 was tested by HPLC (See Figure 2.17a) using a Buckyprep column (10 x 250 mm) eluting with toluene at a flow rate of 4.0 mL/min. Under these conditions compound 4 has a retention time of 17.3 min. ¹H NMR (500 MHz, CS₂/CDCl₃ 4:1, TMS): δ 7.82–7.20 (br, 7 H), 6.30 (s, 4H), 5.72–5.48 (2 d, 1H each one, \(^1J_{(H,H)} = 11.8\) Hz), 4.52 (q, 2H, \(^3J_{(H,H)} = 7.0\) Hz; CH₂), 1.3 ppm (t, 3H, \(^3J_{(H,H)} = 7.0\) Hz; CH₃); MALDI-TOF (positive mode): m/z: 1763.57.

Compound 4 was unstable and readily underwent conversion to 5 (See Figure 2.17); ¹H NMR (500 MHz, CDCl₃, TMS): δ 8.4 (d, 1H, \(^4J_{(H,H)} = 1.8\) Hz; ArH), 8.32 (d, 1H, \(^3J_{(H,H)} = 8.0\) Hz; ArH), 8.30 (br, 2H; ArH), 7.90 (dd, 1H, \(^4J_{(H,H)} = 1.8\) Hz, \(^3J_{(H,H)} = 8.0\) Hz), 7.8 (br, 2H), 5.71 (d, 1H, \(^1J_{(H,H)} = 11.0\) Hz) 5.68 (d, 1H, \(^1J_{(H,H)} = 11.0\) Hz), 4.60 (q, 2H, \(^3J_{(H,H)} = 6.6\) Hz; CH₂), 1.42 ppm (t, 3H, \(^3J_{(H,H)} = 6.6\) Hz; CH₃). MALDI-TOF (positive mode): m/z: 1592.17.
Figure 2.17 Decomposition process of compound 4 followed by HPLC. (Buckyprep column (10 x 250 mm) / Toluene 4.0 mL/min). (a) Compound 4 (b) Solution after 3 hours (c) Compound 5 produced after the decomposition of compound 4.

Figure 2.18 Decomposition process of compound 4 followed by MALDI-TOF spectrometry. (a) The decomposition process of compound 4 begins. (b) The intermediate fraction continues the decomposition process (c) The decomposition process of compound 4 stops when it is converted into compound 5.
Figure 2.19 Conversion of compound 4 into compound 5

It was found that the decomposition process of compound 4 is consequence of an oxidative process, but it is not clear what the oxidating agent is. It is very likely that atmospheric oxygen or the residual water in the solvent is responsible for the oxidation of 4. However, the chemical stability of compound 4 in solution contrasts with that of the equivalent C₆₀ derivative which only decomposes after a few weeks.¹³⁹ Compound 5, containing the anthraquinone moiety, is not interesting for donor acceptor systems because the anthraquinone is also an electron acceptor (See Figure 2.19).

2.2.2. Synthesis of N-methyl-2-exTTF-[5,6]-Sc₃N@I₇-C₈₀

Figure 2.20 Synthesis of 2-exTTF-[5,6]-Sc₃N@I₇-C₈₀
6.3 mg of Sc₃N@I₅-C₈₀ (5.67 µmol, 1 equiv), 28.17 mg of 2-formyl-9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (exTTF-CHO) (68.7 µmol, 12 equiv) and 2.8 mg of N-methyl glycine (sarcosine) (31.4 µmol, 5 equiv) were poured inside a Schlenk flask equipped with a magnetic stirring bar under argon. 50 mL of a 1:1 o-DCB/toluene anhydrous solvent mixture were added to dissolve the materials using a cannula. Once the starting materials were dissolved the reaction mixture was heated up to 120°C using an oil bath while stirring vigorously. The progress of the reaction was followed by TLC using silica plates and eluting first with pure CS₂ to elute the unreacted Sc₃N@I₅-C₈₀; after drying the plates, they were eluted again with a 3:2 mixture of CS₂ and toluene. Once the formation of the bis and poly-adducts was observed the reaction mixture was cooled down to room temperature to stop the reaction and the solvent evaporated under a nitrogen stream in the hood.

Figure 2.21 Purification of N-methyl-2-exTTF-[5,6]-Sc₃N@I₅-C₈₀. Buckyprep column (10 x 250 mm) eluting with toluene 2 mL/min.
The residual yellowish/black solid was re-dissolved with CS$_2$ and eluted through a short neutral alumina column eluting with pure CS$_2$ to recover unreacted Sc$_3$N@$I_k$-C$_{80}$ followed by CS$_2$/toluene mixtures in order to elute the desired product and exTTF-CHO that elutes last with pure toluene. The fraction containing the desired product was dried again and re-dissolved in toluene (HPLC grade) filtered using a Teflon HPLC syringe filter (0.2 µm pore size) and separated by HPLC using a semi preparative Buckyprep column (10 x 250 mm) eluting with toluene 2 mL/min (See Figure 2.21).

![Figure 2.22 500 MHz $^1$H NMR spectrum of N-methyl-2-exTTF-[5,6]-Sc$_3$N@$I_k$-C$_{80}$.](image)

Figure 2.22 500 MHz $^1$H NMR spectrum of N-methyl-2-exTTF-[5,6]-Sc$_3$N@$I_k$-C$_{80}$. 
\(^1\)H NMR (500 MHz, CS\(_2/CD_2Cl_2, \) Residual solvent): \(\delta\) 8.31 (s, 1H; ArH), 7.74 (br, 2H, ArH), 7.61 (br, 2H; ArH), 7.33 (br, 2H), 7.17 (br, 1H), 6.38 (s, 2H, vinyl) 6.36 (br, 1H, vinyl), 6.24 (br, 1H, vinyl), 4.42 ppm (d, 1H, \(^2J_{HH}\) = 9.5 Hz; CH\(_2\)), 3.85 ppm (s, 1H, CH), 3.11 ppm (d, 1H, \(^2J_{HH}\) = 9.5 Hz; CH\(_2\)), 2.53 ppm (s, 3H, CH\(_3\)).

The \(^1\)H NMR spectrum of compound 6 shows the resonances for the protons in the anthracene ring in the region from 8.4 to 7.17 ppm. The vinyl protons in the dithiolene rings are observed between 6.5 and 6.1 ppm, the diastereotopic pyrrolidine protons are observed at 4.42 and 3.11 ppm, respectively. The 9.5 Hz coupling constant has the same magnitude as in the ferrocenyl-[5,6]-pyrrolidines. The remaining pyrrolidine proton is observed at 3.85 ppm and the N-methyl group at 2.53 ppm. The extremely low solubility of compound 6 prevented us from running further NMR experiments. The \(^1\)H NMR spectrum shown in Figure 2.22 was observed after 1024 scans and after suppressing the residual CDHCl\(_2\) signal with a selective irradiation pulse.

2.2.3. Synthesis of N-methyl-2-exTTF-[5,6]-Lu\(_3\)N@I\(_h\)-C\(_{80}\)

![Synthesis of N-methyl-2-exTTF-[5,6]-Lu\(_3\)N@I\(_h\)-C\(_{80}\)](image)

Figure 2.23 Synthesis of N-methyl-2-exTTF-[5,6]-Lu\(_3\)N@I\(_h\)-C\(_{80}\)
3.0 mg of Lu₃N@I₇-C₈₀ (2.0 µmol, 1 equiv), 8.0 mg of 2-formyl-9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (exTTF-CHO) (19.6 µmol, 10 equiv) and 1.2 mg of N-methyl glycine (sarcosine) (11.5 µmol, 11.5 equiv) were poured inside a Schlenk flask equipped with a magnetic stirring bar under argon. 20 mL of anhydrous chlorobenzene was added and stirring started. The reaction mixture was heated to reflux using an oil bath. The progress of the reaction was followed by TLC using silica plates and eluting first with pure CS₂. The unreacted Sc₃N@I₇-C₈₀ eluted with the front of the solvent and compound 7 elutes with a 3:2 mixture of CS₂ and toluene. Once the formation of the bis and poly-adducts was observed the reaction mixture was removed from the bath to stop the reaction and the solvent evaporated under a nitrogen stream in the hood. Following the same process used for purifying the Sc₃N@I₇-C₈₀ derivative, the residual yellowish/black solid was re-dissolved with CS₂ and separated using a short neutral alumina column, first eluting with pure CS₂ to recover un-reacted Sc₃N@I₇-C₈₀ followed by CS₂/toluene mixtures in order to elute the desired product and exTTF-CHO was recovered by elution with pure toluene. The fraction containing the desired product was dried again and re-dissolved in toluene (HPLC grade) filtered using a Teflon HPLC syringe filter (0.2 µm pore size) and separated by HPLC using a semi preparative PBB column (4.6 x 250 mm) eluting with toluene 2.0 mL/min. ¹H NMR (500 MHz, CS₂/CD₂Cl₂, Residual solvent): δ 8.40 (s, 1H; ArH), 7.80 (br, 2H, ArH), 7.65 (br, 2H; ArH), 7.32 (br, 2H), 7.23 (br, 1H), 6.47 (br, 2H, vinyl) 6.45 (br, 1H, vinyl), 6.30 (br, 1H, vinyl), 4.42 ppm (d, 1H, ²J(H,H) = 9.5 Hz; CH₂), 3.82 ppm (s, 1H, CH), 3.05 ppm (d, 1H, ²J(H,H) = 9.5 Hz; CH₂), 2.60 ppm (s, 3H, CH₃).
Figure 2.24 HPLC purification of N-methyl-2-exTTF-[5,6]-Lu$_3$N@I$_h$-C$_{80}$. PBB column (4.6 x 250 mm) mobile phase toluene 2.0 mL/min.

Figure 2.25 MALDI-TOF mass spectrum of N-methyl-2-exTTF-[5,6]-Lu$_3$N@I$_h$-C$_{80}$

The $^1$H NMR spectrum of compound 7 is completely analogous to that of compound 6 with differences in the chemical shifts of only a few Hertz. Both of these compounds are way more stable than the exTTF-Bingel derivative of Y$_3$N@I$_h$-C$_{80}$, indicating that
either the encapsulated metal, the connectivity [5,6] vs [6,6] or the purification method is related to the chemical stability of these compounds in solution.

2.3. Phthalocyanine based dyads

Phthalocyanines are aromatic macrocycles analogous to porphyrins. Phthalocyanines have outstanding optical properties particularly high extinction coefficients in the red - near infrared spectral region, one of the most important of the solar spectrum; hence they have emerged as attractive materials for the construction of artificial photosynthetic antennas for harvesting solar energy. Phthalocyanines have been successfully used in the construction of donor acceptor systems with fullerenes and as TiO$_2$ photosensitizers for the construction of dye sensitized solar cells.

2.3.1. Synthesis of 81-ethyl-[tri-tert-butylhydroxymethyloxycarbonylphthalocyaninato-zinc(II)]-81-(ethoxy-carbonyl)-[6,6]-Y$_3$N@I$_n$-C$_{80}$fullerene

![Figure 2.26 Synthesis of 81-ethyl-[tri-tert-butylhydroxymethyloxycarbonylphthalocyaninato-zinc(II)]-81-(ethoxy-carbonyl)-[6,6]-Y$_3$N@I$_n$-C$_{80}$fullerene.](image)
2-bromo-ethyl-[tri-*tert*-butylhydroxymethylphthalocyaninato-zinc(II)] malonate 8 was prepared in three steps starting with tri-*tert*-butylformylphthalocyaninatozinc(II) (Pc-CHO). The starting aldehyde was first reduced, the resulting alcohol was esterified and the obtained malonate was mono-brominated. The starting Pc-CHO was provided by Professor Tomás Torres. 0.82 mg (0.66 µmol, 1 eq) of Y₃N@C₈₀ and 1.60 mg (1.72 µmol, 2.6 eq) of compound 8 were poured in a Schlenk flask equipped with a magnetic stirring bar. The flask was purged of air and filled with argon. 3.0 mL of *o*-DCB were transferred using a cannula and stirring was started. 1.0 µL of DBU was added by using an HPLC syringe and the reaction mixture stirred for 4 hours. The reaction mixture was purified by preparative TLC. The plate was eluted with CS₂ in order to remove unreacted Y₃N@Iₘ-C₈₀, which elutes with the solvent front.

![Figure 2.27 HPLC traces](image)  
Figure 2.27 HPLC traces of (a) Y₃N@Iₘ-C₈₀ (b) Compound 9 (c) Final product after decomposition. Buckyclutcher column (10 x 250 mm) eluting with toluene 4.0 mL/min
There was a spot with an Rf value of 0.3 corresponding to the \( \text{Y}_3 \text{N}\text{I}_9 \text{C}_{80} \text{-monoethylmalonic acid adduct} \) [MALDI-TOF \( m/z \) (positive mode) 1253.96 (base peak), 1298 \( M^+-(\text{CH}_3\text{CH}_2\text{-CO}_2) \) no molecular peak was observed, it had an 8.13 min retention time on HPLC (Buckyclutcher, toluene 4 mL/min)]. The desired product 9 barely moved on the silica plate, but when the plate was eluted with \( \text{CH}_2\text{Cl}_2 \) compound 9 moved with the solvent front. Compound 9 has a 9.50 min retention time (Buckyclutcher, toluene 4.0 mL/min). MALDI-TOF \( m/z \) 2125.81. It was not possible to obtain NMR data for this compound because it converted after few hours into \( \text{Y}_3 \text{N}\text{I}_9 \text{C}_{80} \text{-monoethylmalonic acid} \) (See Figure 2.27).

### 2.3.2. Synthesis of 2-TPA-Phth-[5,6]-Sc\(_3\)N\text{I}_9-C\(_{80}\)-fulleropyrrolidine

![Synthesis of 2-TPA-Phth-[5,6]-Sc\(_3\)N\text{I}_9-C\(_{80}\)-fulleropyrrolidine](image)

Figure 2.28 Synthesis of 2-TPA-Phth-[5,6]-Sc\(_3\)N\text{I}_9-C\(_{80}\)-fulleropyrrolidine

6.1 mg of \( \text{Sc}_3\text{N}\text{I}_9 \text{C}_{80} \) (5.5 µmol, 1 equiv), 50.0 mg of compound 10 (48.0 µmol, 8.7 equiv) and 4.2 mg of \( N \)-methyl glycine (sarcosine) (46.8 µmol, 8.5 equiv) were poured inside a Schlenk flask equipped with a magnetic stirring bar under argon. 50 mL of a 4:1
o-DCB/DMF anhydrous solvent mixture were added to dissolve the materials using a cannula. This reaction mixture was heated up to 130°C using an oil bath while stirring for two hours. The progress of the reaction was followed by TLC using silica plates and eluting first with pure CS$_2$ to elute the un-reacted Sc$_3$N@I$_{p}$-C$_{80}$ followed by a 1:2 mixture of CS$_2$ and toluene. Once the formation of the bis and poly-adducts was observed the reaction mixture was removed from the heat to stop the reaction and the solvent evaporated under a nitrogen stream. The residual greenish/black solid was re-dissolved with CS$_2$ and eluted through a short silica column eluting first with pure CS$_2$ to recover un-reacted Sc$_3$N@I$_{p}$-C$_{80}$ followed by CS$_2$/toluene mixtures in order to elute the desired product. The fraction eluted with toluene/CS$_2$ 2:1 contained the desired product (See Figure 2.29a).

![Figure 2.29 Purification of 2-TPA-Phth-[5,6]-Sc$_3$N@I$_{p}$-C$_{80}$-fulleropyrrolidine](image)

Part of compound 10 was recovered from the column by eluting with Toluene/Ethyl acetate 3:1 mixture. The fraction containing the desired product was dried and re-
dissolved in toluene (HPLC grade) filtered using a Teflon HPLC syringe filter (0.2 µm pore size) and separated by HPLC using a semi preparative PBB column (4.6 x 250 mm) (See Figure 2.29). \(^1\)H NMR (500 MHz, CS\(_2\)/CD\(_2\)Cl\(_2\) 3:2, Residual solvent): \(\delta\) 7.70 (d, 2H \(^3\)J\(_{HH}\) = 9.0 Hz; ArH), 7.48 - 7.35 (m, 9H, ArH), 7.29 – 7.20 (m, 4H; ArH), 7.19 – 7.05 (br, 10H, ArH), 4.35 ppm (d, 1H, \(^2\)J\(_{HH}\) = 9.5 Hz; CH\(_2\)), 3.79 ppm (s, 1H, CH), 3.08 ppm (d, 1H, \(^2\)J\(_{HH}\) = 9.5 Hz; CH\(_2\)), 2.65 ppm (s, 3H, CH\(_3\)), 1.29 ppm (s, 27H, -C(CH\(_3\))\(_3\)).

![Figure 2.30 500 MHz \(^1\)H NMR spectrum of 2-TPA-Phth-[5,6]-Sc\(_3\)N@I\(_{80}\)-C\(_{50}\)-fulleropyrrolidine.](image-url)
3. Electrochemical properties

All electrochemical measurements were performed in a 0.050 M solution of tetra(n-butyl)ammonium hexafluorophosphate (nBu₄NPF₆) in o-DCB. Voltammetric experiments were performed using a potentiostat/galvanostat Model CHI660A (CH Instruments Electrochemical Workstation) with a three-electrode cell placed in a Faraday cage. The working electrode consisted of a glassy carbon disk (Bioanalytical Systems, Inc.) with a diameter of 1 mm. The surface of the electrode was polished using 0.25 µm diamond polishing compound (Metadi II, Buehler). The electrode was then sonicated in water in order to remove traces of alumina from the metal surface, washed with deionized water, and dried. A silver wire was used as pseudo-reference electrode and ferrocene added as internal standard for calibrating the redox potentials.

The electrochemical properties of the compounds were measured and compared to those of the pristine TNT-EMFs, C₆₀ and TNT-EMF-fulleropyrrolidine derivatives without a donor moiety for comparison. The redox potentials were collected and are listed in Table 2. The reductive electrochemical behavior of the pristine M₃N@I₇-C₈₀ (M=Sc, Lu, Y) at scan rates of 100 mV/s is chemically reversible but electrochemically irreversible, although in the case of Sc₃N@I₇-C₈₀ it can be reversible at high scan rates.¹⁹,²⁰ All the [5,6]-M₃N@I₇-C₈₀ (M=Sc, Lu) derivatives prepared have reversible reductive electrochemical behavior (See Figure 2.31) contrary to the pristine TNT-EMFs which have chemically reversible, but electrochemically irreversible reductive electrochemistry.⁶² The [6,6]-Y₃N@I₇-C₈₀ compounds, on the other hand, have irreversible electrochemical behavior. These results are consistent with the previously
observed trend. The ferrocenyl derivatives of $M_3N@I_{16-C_{80}}$ (M = Sc, Y) (Figure 2.31 traces b and f respectively) display irreversible oxidation processes close to 0 V vs Fc/Fc⁺. The irreversibility may be related to the retro-cycloaddition reaction. Perhaps the oxidation of the addend promotes or catalyzes the decomposition of the fulleropyrroline producing again the pristine fullerene. The remaining oxidation processes occur on the fullerene cage, but the second oxidation of the fullerene is not always observed due to limitations in the potential window.

Figure 2.31 Cyclic voltammograms of (a) Sc$_3$N@I$_{16-C_{80}}$ (b) Compound 1 (c) Compound 6 (d) Compound 7 (e) Y$_3$N@I$_{16-C_{80}}$ (f) Compound 2 (g) Compound 4 (h) Compound 5. Supporting electrolyte $n$Bu$_4$NPF$_6$ 0.050 M in o-DCB. Scan rate 100 mV/s, glassy carbon working electrode, Pt counter, Ag wire as reference.
The oxidative process for the \textit{ex}TTF derivatives of M\textsubscript{3}N@I\textsubscript{h}-C\textsubscript{80} (M = Sc, Y, Lu) (Figure 2.31 traces c, g and d respectively) display addend based irreversible oxidation processes at +0.23 V for the Y, +0.32 for Sc and 0.17 for the Lu derivative. Such differences are probably due to both different connectivity patterns ([6,6]-Bingel for Y vs [5,6]-pyrrolidine for Sc and Lu) and different metal clusters. The remaining oxidation processes again correspond to the oxidations on the fullerene cage.

Table 2.1 Redox potentials of TNT-EMF donor acceptor systems compared to C\textsubscript{60}, pristine TNT-EMFs and some TNT-EMF derivatives used as references. All the values are reported in volts vs the Fc/Fc\textsuperscript{+} redox pair. Supporting electrolyte nBu\textsubscript{4}NPF\textsubscript{6} 0.050 M in o-DCB. Scan rate 100 mV/s, glassy carbon working electrode, Pt counter, Ag wire as reference.

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<th>Compound</th>
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<th>Addend Based $E^{0/+}$</th>
<th>Cage Based $E^{0/-}$</th>
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<th>E\textsubscript{0/-}</th>
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<td>+0.60</td>
<td>-</td>
<td>-1.43</td>
<td>-2.89</td>
<td>-</td>
<td>2.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compound 1</td>
<td>+1.09</td>
<td>+0.61</td>
<td>+0.15</td>
<td>-1.14</td>
<td>-1.53</td>
<td>-2.25</td>
<td>1.29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compound 2</td>
<td>+0.66</td>
<td>+0.57</td>
<td>+0.07</td>
<td>-1.41</td>
<td>-1.77</td>
<td>-</td>
<td>1.48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compound 4</td>
<td>+0.90</td>
<td>-</td>
<td>+0.23</td>
<td>-1.28</td>
<td>-1.77</td>
<td>-2.22</td>
<td>1.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compound 5</td>
<td>-</td>
<td>+0.67</td>
<td>-</td>
<td>-1.34</td>
<td>-1.72</td>
<td>-</td>
<td>2.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compound 6</td>
<td>+0.99</td>
<td>+0.69</td>
<td>+0.32</td>
<td>-1.11</td>
<td>-1.51</td>
<td>-2.22</td>
<td>1.43</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compound 7</td>
<td>+1.10</td>
<td>+0.47</td>
<td>+0.17</td>
<td>-1.23</td>
<td>-1.57</td>
<td>-2.26</td>
<td>1.40</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The electrochemical behavior of compound 5 was studied and compared with that of 2-hydroxymethylanthraquinone. The presence of two new reduction reversible waves further confirmed the conversion of compound 4 into compound 5. It was not possible to study the electrochemical properties of compound 9 due to the hydrolysis process. However, the electrochemical properties of compound 11 revealed the presence of a new addend based reduction process in addition to the 3 reduction steps occurring on the fullerene cage. The second and the fourth reduction processes are two electron processes where one of the electrons is presumably added to the fullerene cage and the other to the phthalocyanine addend (See Figure 2.32).

Figure 2.32 CVs of Phthalocyanine derivatives (a) Pristine Sc$_2$N@I$_6$-C$_{80}$ (b) Compound 10 used as reference (c) Compound 11. Supporting electrolyte $n$Bu$_4$NPF$_6$ 0.050 M in $o$-DCB. Scan rate 100 mV/s, glassy carbon working electrode, Pt counter, Ag wire as reference.
The third reduction potential at -1.83 is probably phthalocyanine based. In the oxidation side, the first oxidation process at +0.37 V is probably due to the retro-cycloaddition reaction, the second oxidation is occurring on the phthalocyanine and the third process on the fullerene cage. The redox potentials of compounds 10 and 11 are collected in Table 2.2

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cage Based</th>
<th>Addend Based</th>
<th>Cage Based</th>
<th>Addend Based</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc$_3$N@I$<em>h$-C$</em>{80}$</td>
<td>+1.09</td>
<td>+0.59</td>
<td>-1.26</td>
<td>-1.62</td>
</tr>
<tr>
<td>Phth-TPA-CHO (10)</td>
<td>-</td>
<td>+0.76</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Compound 11</td>
<td>+0.99</td>
<td>+0.37</td>
<td>-1.09</td>
<td>-1.46</td>
</tr>
</tbody>
</table>

The reduction potential values are important because the open circuit voltages in the organic solar cells are proportional to the energy difference between the HOMO of the donor and the LUMO of the acceptor. As a consequence, derivatives with higher reduction potential will produce organic solar cells with larger open circuit voltages hence higher efficiencies. All the prepared TNT-EMF donor acceptor systems have higher reduction potentials than their C$_{60}$ counterparts thus the utilization of TNT-EMFs have the potential to increase the open circuit voltages of organic solar cells and thus the efficiencies. Actually, it was reported that when the phenyl-C$_{81}$-butyric acid hexyl ester of Lu$_3$N@I$_h$-C$_{80}$ (PCBH-Lu$_3$N@I$_h$-C$_{80}$) was mixed with P3HT, bulk heterojunction
organic solar cells with higher open circuit voltages were obtained yet the efficiency was limited by the conductance of the material.\textsuperscript{67,122}

3.1. Influence of the [5,6] vs [6,6] addition pattern

The electrochemical differences of the [5,6] vs [6,6] TNT-EMF donor acceptor systems is particularly important due to the intended applications. Derivatives with reversible electrochemical behavior would be analogous to the fullerene derivatives used today for the fabrication of bulk heterojunction solar cells.\textsuperscript{155} An irreversible reductive electrochemical behavior may affect the mobility of the electrons, once the charges are separated by light. The electrons may be trapped in the fullerenes instead of efficiently hopping through the material until the cathode is reached. The reductive electrochemical behavior of M\textsubscript{3}N@I\textsubscript{h}-C\textsubscript{80} (M = Sc, Y, Er, Lu) derivatives is correlated with the position of the addend. The regioselectivity is controlled by the nature of the metal cluster inside the fullerene cage.\textsuperscript{28,37,38} The [6,6] pyrrolidine derivatives of Sc\textsubscript{3}N@I\textsubscript{h}-C\textsubscript{80} are particularly difficult to prepare because Sc\textsubscript{3}N@I\textsubscript{h}-C\textsubscript{80} has a preference for the [5,6] regioisomers and in the cases where the [6,6] fulleropyrrolidine regioisomer is obtained it readily isomerizes to the [5,6] upon heating.\textsuperscript{35} The electrochemical behavior of the [6,6]-Sc\textsubscript{3}N@I\textsubscript{h}-C\textsubscript{80} had never been reported so we reproduced the synthesis of the only [6,6]-Sc\textsubscript{3}N@I\textsubscript{h}-C\textsubscript{80} fulleropyrrolidine that has been successfully prepared\textsuperscript{135} and studied its electrochemical properties. Simultaneously, analogous compounds were prepared using Lu\textsubscript{3}N@I\textsubscript{h}-C\textsubscript{80} because of its high reduction potential and its consequent promise as an effective TNT-EMF for the construction of organic solar cell devices.\textsuperscript{13}C enriched N-
triphenylmethyl-5-oxazolidinone\textsuperscript{156} (See Figure 2.33) was used to prepare the [5,6] and [6,6] fulleropyrrolidines of M\textsubscript{3}N@I\textsubscript{h}-C\textsubscript{80} (M = Sc, Lu). The products of both reactions were separated by two stage HPLC chromatography starting with a Buckyprep column and completing the process with a Buckyclutcher column. Toluene was used as mobile phase.

![Figure 2.33 1H-13C-HMBC spectrum of N-triphenylmethyl-5-oxazolidinone](image.png)
The regioselectivity of the addition was easily followed by $^{13}$C NMR experiments because the [5,6] derivatives have a symmetry plane bisecting the molecule perpendicular to the plane of the paper (See Figure 2.34); thus only one $^{13}$C signal is observed for the methylene carbons in the pyrrolidine ring. On the other hand, due to the loss of symmetry for the [6,6] derivatives two $^{13}$C signals are observed. When comparing the chemical shifts of the methylene carbons in the pyrrolidine ring (See Table 2.3), the [5,6]-regioisomers have a difference of almost ~5.7 ppm. Such a drastic difference caused by the metal in the trimetallic cluster has not been observed before.

In the [5,6] regioisomers those methylene carbons are connected to corannulene type carbons, thus it clearly indicates that the trimetallic cluster trapped in the fullerene cage is interacting differently with them and this can help to explain the preference for the formation of different regioisomers depending on the encapsulated metal because the electronic density in the corannulene type carbons vs the pyrene type is clearly different.
Table 2.3 $^{13}$C NMR chemical shifts of the methylene carbons in the pyrrolidine ring of the $N$-trityl-[5,6] and [6,6]-M$_3$N@I$_{60}$-C$_{80}$ (M = Sc, Lu) fulleropyrrolidines. All the spectra were recorded using a saturated solution of Chromium (III) acetylacetonate in CS$_2$ as solvent with an external acetone-d$_6$ capillary tube for lock and referencing. Relaxation delay 100 mS; typically between 30,000 to 50,000 scans were required.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Methylene linked to corannulene type carbon $\delta$ (ppm)</th>
<th>Methylene linked to pyrene type carbon $\delta$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound 12</td>
<td>62.58</td>
<td>-</td>
</tr>
<tr>
<td>Compound 14</td>
<td>68.29</td>
<td>-</td>
</tr>
<tr>
<td>Compound 13</td>
<td>65.59</td>
<td>57.58</td>
</tr>
<tr>
<td>Compound 15</td>
<td>62.35</td>
<td>56.24</td>
</tr>
</tbody>
</table>

Figure 2.35 Cyclic voltammograms of $N$-triphenylmethyl-[5,6] and [6,6]-M$_3$N@I$_{60}$-C$_{80}$ fulleropyrrolidines (M= Sc, Lu). All the values are reported in volts vs the Fc/Fc$^-$ redox pair. Supporting electrolyte nBu$_4$NPF$_6$ 0.050 M in $o$-DCB. Scan rate 100 mV/s, glassy carbon working electrode, Pt counter, Ag wire as reference.
The reductive electrochemical behavior of the \textit{N}-triphenylmethyl-[5,6]-M$_3$N@I$_{h}$-C$_{80}$ (M = Sc, Lu) was found to be reversible at normal scan rates (100 mV/s) and irreversible for the \textit{N}-triphenylmethyl-[6,6]-Lu$_3$N@I$_{h}$-C$_{80}$. Surprisingly the reductive electrochemical behavior of \textit{N}-triphenylmethyl-[6,6]-Sc$_3$N@I$_{h}$-C$_{80}$ is also reversible (See Figure 2.35c) and the second reduction occurs more easily than for the [5,6] regioisomer. There is no significant difference for the third reduction process, thus the energy difference between the second and third reduction process, which represents the energy difference between the LUMO +1 and LUMO +2, is bigger.

Table 2.4 Redox potentials of \textit{N}-trityl [5,6] and [6,6] fulleropyrroldines of M$_3$N@I$_{h}$-C$_{80}$ (M = Sc, Lu). All the values are reported in volts vs the Fc/Fc$^+$ redox pair. Supporting electrolyte nBu$_4$NPF$_6$ 0.050 M in o-DCB. Scan rate 100 mV/s, glassy carbon working electrode, Pt counter, Ag wire as reference.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cage Based</th>
<th>Retro Cycloaddition</th>
<th>Cage Based</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E^{+/+2}$</td>
<td>$E^{0/+}$</td>
<td>$E^{0/+}$</td>
</tr>
<tr>
<td>Sc$<em>3$N@I$</em>{h}$-C$_{80}$</td>
<td>+1.09</td>
<td>+0.59</td>
<td>-</td>
</tr>
<tr>
<td>Lu$<em>3$N@I$</em>{h}$-C$_{80}$</td>
<td>+1.11</td>
<td>+0.64</td>
<td>-</td>
</tr>
<tr>
<td>[5,6]-Sc$<em>3$N@I$</em>{h}$-C$_{80}$</td>
<td>+1.00</td>
<td>+0.68</td>
<td>+0.35</td>
</tr>
<tr>
<td>[6,6]-Sc$<em>3$N@I$</em>{h}$-C$_{80}$</td>
<td>+1.12</td>
<td>+0.65</td>
<td>+0.41</td>
</tr>
<tr>
<td>[5,6]-Lu$<em>3$N@I$</em>{h}$-C$_{80}$</td>
<td>-</td>
<td>+0.65</td>
<td>+0.30</td>
</tr>
<tr>
<td>[6,6]-Lu$<em>3$N@I$</em>{h}$-C$_{80}$</td>
<td>-</td>
<td>+0.70</td>
<td>+0.50</td>
</tr>
</tbody>
</table>

This result adds evidence to the fact that contrary to other TNT-EMFs,\textsuperscript{7,62,74} Sc$_3$N@I$_{h}$-C$_{80}$ has very different chemical and electrochemical properties.
4. Conclusions and Recommendations

The purification process for Sc$_3$N@I$_x$-C$_{80}$ previously developed by our group,$^{20}$ was improved and standardized and allowed the purification of multi-milligram quantities of Sc$_3$N@I$_x$-C$_{80}$ in short times. The preparation of TNT-EMF donor acceptor systems was successfully achieved. Unfortunately, the chemical and thermal stability of the obtained compounds is low.

The synthesis of the most stable derivative (Compound 1) was scaled up and a 5.0 mg sample of the material was sent to Professor’s Dirk Guldi research group in order to study the photophysical properties of this novel dyad. Professor’s Guldi research group obtained very encouraging results. The lifetime of the radical pair charge separated state formed upon light irradiation is ~three times longer than the equivalent C$_{60}$ donor acceptor system (Compound 7 is currently under investigation in Professor’s Guldi lab). Thus the preparation of donor acceptor dyads with better donor systems is desirable in order to see whether or not, it is possible to surpass the lifetime of the best C$_{60}$ based dyads known.

A bigger sample (50.0 mgs) of compound 1 was prepared and sent to Luna Nanoworks Inc. for constructing an organic solar cell device, but the solubility of the compound (<2.0 mg/mL of o-DCB) is too low for the fabrication process where solubilities of ~20 mg/mL of fullerene derivative in o-DCB are required. Thus the incorporation of bigger functional groups capable of enhancing the solubility without affecting the conductance properties is required.
The fabrication of organic solar cell devices is currently dominated by the bulk heterojunction technology and the incorporation of molecular junctions seems complicated because the formation of the $n$-type and $p$-type phases is required for the correct operation of the cell. Thus donor acceptor systems have to be designed not only considering the electronic and physical properties, but also they have to incorporate the ability to self assemble into functional systems.
1. Introduction

The efficiency and the lifetime of the charge separated states formed in the covalent donor acceptor systems upon light irradiation are strongly dependent on the nature and length of the spacer group. Several strategies have been implemented to connect the donor and the acceptor molecules. In the most common, the donor and the acceptor are linked by an aliphatic bridge. Aliphatic linkers behave as insulators because their LUMO orbitals are high in energy and cannot be accessed easily; hence, they inhibit the electron transport. In those systems energy transfer takes place mainly through a Förster resonance mechanism\textsuperscript{157} and the lifetime of the charge separated state increases with the length of the bridge. However, the overall efficiency of the process decays exponentially with the separation distance between the donor and the acceptor.\textsuperscript{158,159} Rigid bridges are preferred because different conformers of the same molecule may exhibit different behavior so the final outcome is hard to predict.

Another alternative to connect the donor and acceptor is to create a redox gradient by connecting several electro active centers that can give rise to short electron transfer events that end up with a radical pair separated by a long distance.\textsuperscript{101,160} This strategy is analogous to the natural photosynthetic process, and radical pairs separated by distances of up to 50 Å have been prepared. These values are outstanding compared to the 20 Å limit for the donor acceptor systems connected with aliphatic bridges. The main
disadvantage of this strategy is that some energy is lost in every redox step through the gradient.

The donor and the acceptor systems can also be connected with highly conjugated linkers. The strong electronic delocalization in the linker makes them behave as molecular wires. The electron transfer process depends on the degree of electronic coupling between the donor, linker and acceptor orbitals because the charge separation and charge recombination involves the orbitals of the linker.\textsuperscript{121} A full electronic delocalization is not convenient because the radical pair can easily recombine thus the conjugation is usually disrupted or modulated to stabilize the charge separated states. More recent alternatives to the construction of donor acceptor systems use combinations of the previously described methods or supramolecular chemistry. In the latter case, the donor and acceptor moieties are linked using catenanes\textsuperscript{161} or $\pi$-$\pi$ interactions.\textsuperscript{143,162}

Here we describe the preparation of five $\text{Sc}_3\text{N}@$$I_8$-$\text{C}_{80}$ fulleropyrrolidines in order to evaluate both the effect of the substitution and the length of the linker in the lifetime of the charge separated states. Part of the experimental procedures and graphs presented here are a pre-peer reviewed version of the following article (See Appendix C for the copyright letter):

2. Synthesis of the Compounds

The most successful strategy in the previous studies (1,3-dipolar cycloaddition reaction) was applied to the preparation of two different sets of donor acceptor systems. In the first case triphenylamine was chosen as the donor system in order to study the effect of the substitution pattern (2-substituted vs N-substituted-[5,6]-Sc$_3$N@I$_h$-C$_{80}$ fulleropyrrolidines) in the thermal stability of the donor acceptor systems and the effect on the lifetime of the charge separated states. In the second case, the length of the linker in a series of paracyclopheane linked porphyrin donor acceptor systems was studied.

2.1. Triphenylamine (TPA) based dyads

Triphenylamine and its derivatives have been successfully employed as donor systems in the construction of small molecule donor - solution processable organic solar cells,$^{163-167}$ TiO$_2$ dye sensitized solar cells,$^{168-170}$ and fullerene donor acceptor conjugates.$^{171-174}$ Although TPA derivatives are not good absorbers in the visible range, they are good donors and have excellent hole transporting properties.$^{175}$ They have a propeller structure that is advantageous for the solution processability because after the evaporation of the solvent they produce highly homogeneous thin films.$^{164}$ Finally, they have the ability to form and stabilize cation radicals.$^{176}$

Based on all these interesting properties we chose TPA for the substitution studies. 4-(diphenylamino)benzaldehyde was obtained from Aldrich and purified by column chromatography before use. Sc$_3$N@I$_h$-C$_{80}$ was purified as previously described using the selective oxidative method.$^{20}$
2.1.1. Synthesis of $N$-methyl-2-(4-diphenylaminophenyl)-[5,6]-$I_h$-$Sc_3N@C_{80}$-fulleropyrrolidine

![Figure 3.1 Synthesis of $N$-methyl-2-(4-diphenylaminophenyl)-[5,6]-$I_h$-$Sc_3N@C_{80}$-fulleropyrrolidine](image)

9.82 mg of $Sc_3N@I_h$-$C_{80}$ (8.85 µmol, 1 eq) was poured in a 100 mL Schlenk flask along with 121.80 mg of 4-(diphenylamino)benzaldehyde (445 µmol, 50 eq) and 11.48 mg of sarcosine (128.85 µmol, 14.5 eq). The solids were dissolved in 50 mL $o$-dichlorobenzene and heated to 120°C under argon for 90 minutes and the progress of the reaction followed by TLC using silica plates eluting with CS$_2$/Toluene 2:1. Once the formation of bis and poly adducts was observed in the plates, the flask was removed from the heating bath to stop the reaction and the solvent removed under high vacuum. The remaining solid was then dissolved in CS$_2$ and purified on a silica gel column eluting first with CS$_2$ for removing the unreacted $Sc_3N@I_h$-$C_{80}$ followed by a 1:1 mixture of CS$_2$ and toluene for eluting the product. After evaporating the solvent and washing with ethyl ether, 5.15 mg of product were obtained. (40.6% yield). This compound has retention time 26.73 min on a Buckyprep column (10 x 250mm) - toluene 2 mL/min. $^1$H NMR (500 MHz, CS$_2$/CD$_2$Cl$_2$ 4:1) δ 7.92 broad (s, 2H, ArH), 7.38 broad (s, 2H, ArH), 7.30 (t,
4H, \(^3J_{(H,H)}=7.5\) Hz, ArH), 7.18 (d, 4H, \(^3J_{(H,H)}=7.5\) Hz, ArH), 7.04 (t, 2H, \(^3J_{(H,H)}=7.5\) Hz, ArH), 4.35 (d, 1H, \(^2J_{(H,H)}=9\) Hz, CH\(_2\)), 3.74 (s, 1H, CH), 3.06 (d, 1H, \(^3J_{(H,H)}=9\) Hz, CH\(_2\)), 2.63 (s, 3H, CH\(_3\)). MALDI \(m/z\) 1411.97 (negative ionization, 9-nitroanthracene as matrix).

Figure 3.2 500 MHz \(^1\)H NMR spectrum of \(N\)-methyl-2-(4-diphenylaminophenyl)\{-5,6\}-\(I_n\)-SnN@C\(_{80}\) fulleropyrrolidine
The $^1$H NMR spectrum of compound 16 (See Figure 3.2) shows broad resonances at 7.92 and 7.38 ppm for the protons in the aromatic ring directly connected to the pyrrolidine because the rotation of the addend is hindered by the fullerene cage.\textsuperscript{177}

2.1.2. Synthesis of \(N\)-(benzyl-4-diphenylaminophenyl)-[5,6]-Sc$_3$N@\(I_b\)-C$_{80}$ fulleropyrrolidine

\[ \text{1. Glycine methyl ester} + \text{HCl} \rightarrow \text{NaBH}_3\text{CN}, \text{EtOH, 60°C} \]
\[ \text{2. NaOH, EtOH/Water 60°C stirring overnight} \]

Figure 3.3 Synthesis of \(N\)-(benzyl-4-diphenylaminophenyl)-[5,6]-Sc$_3$N@\(I_b\)-C$_{80}$ fulleropyrrolidine

\(N\)-(benzyl-4-diphenylaminophenyl)glycine 17 was prepared as follows: 352.0 mg of 4-(diphenylamino)benzaldehyde (1.29 mmol, 1 eq) and 326.0 mg of glycine methyl ester hydrochloride (2.59 mmol, 2 eq) were poured in a 200 mL Schlenk flask equipped with a stirring bar under argon. 100 mL of anhydrous ethanol was added, the stirring started and the mixture heated to 60°C. Once the starting materials were dissolved the solution turned to a yellowish color. At that point dropwise addition of NaBH$_3$CN (0.705 g, 11.2 mmol, 3 eq) suspended in anhydrous ethanol was started and continued for a period of 3 hours. Finally the solvent was removed under vacuum and the residual solid treated with
5% HCl solution to destroy the excess of NaBH₃CN. A saturated NaHCO₃ solution was added dropwise until a neutral pH was reached. The whole mixture was extracted with CH₂Cl₂, dried with anhydrous Na₂SO₄ and the solution filtered through a silica plug to remove the polymeric brown material. After evaporating the solvent the intermediate ester was obtained and used in the next step without further purification. ¹H NMR (500 MHz, CD₂Cl₂, TMS) δ 7.34-7.28 (m, 6H, ArH), 7.16-7.04 (m, 8H, ArH), 3.84 (s, 2H, BzH), 3.78 (s, 3H, -O-CH₃), 3.51 (s, 2H, N-CH₂-CO). ¹³C NMR (125 MHz, CD₂Cl₂, TMS) δ 172.6 carbonyl, 147.9 q, 146.9 q, 134.1 q, 129.3 CH, 129.2 CH, 124.2 CH, 124.1 CH, 122.7 CH, 52.5 φ-CH₂-N, 51.6 -O-CH₃ and 49.7 N-CH₂COO. This compound was dissolved in 20 mL of ethanol-water 8:1 and a 0.20 mL of saturated NaOH solution was added. The whole mixture was heated to 60 °C and stirred overnight. The final reaction mixture was cooled with ice and HCl 5% added dropwise until a neutral pH was reached, which precipitated the product out of the solution. The white solid obtained was washed with cold de-ionized water and dried under vacuum. 98.5 mg of product was obtained (23% yield). ¹H NMR (500 MHz, DMSO, Residual solvent) δ 9.57 (br, 1H, -COOH), 7.42 (d, 2H, ³J(H,H)= 9 Hz), 7.32 (t, 4H, ³J(H,H)= 7.5 Hz), 7.08 (t, 2H, ³J(H,H)= 7.5 Hz), 7.02 (d, 4H, ³J(H,H)= 7.5 Hz), 6.97 (d, 2H, ³J(H,H)= 9Hz), 4.08 (s, 2H), 3.81 (s, 2H), 3.38 (br, 1H, NH). ¹³C NMR (125 MHz, DMSO, Residual solvent) 167.8 carbonyl, 148.0 q, 146.9 q, 131.6 CH, 129.6 CH, 125.0 q, 124.3 CH, 123.5 CH, 122.5 CH, 49.3 φ-CH₂-N, 46.1 N-CH₂COO. (See Figure 3.4) In the last step 12.1 mg of Sc₃N@I₉-C₈₀ (10.9 µmol, 1 eq) was poured in a 100 mL Schlenk flask along with 34.5 mg of N-(benzyl-4-
diphenylaminophenyl)glycine (109.1 µmol, 10 eq) and 40 mL of anhydrous o-
dichlorobenzene were added by using a cannula.

Figure 3.4 $^1$H-$^{13}$C HMBC spectrum of N-(benzyl-4-diphenylaminophenyl)glycine

This mixture was heated to 150°C under argon and a slurry made with paraformaldehyde (24.5 mg, 816 µmol, 75 eq) in 10 mL of anhydrous o-DCB was added in 3 portions every 15 minutes; heating was continued while following the reaction by TLC on silica plates eluting with CS$_2$-toluene 2:1. The reaction was stopped when the formation of bis and polyadducts was observed in the TLC plates even though the starting
Sc$_3$N@$I_h$-C$_{80}$ had not been consumed completely. The solvent was then removed under high vacuum and the remaining solid dissolved in CS$_2$ and purified on a silica gel column eluting first with CS$_2$ for removing the un-reacted Sc$_3$N@$I_h$-C$_{80}$ followed by a 1:1 mixture of CS$_2$ and toluene for eluting the product. After evaporating the solvent and washing with ethyl ether 5.50 mg of product was obtained. (38.5% yield, 43.8% calculated based on the consumed Sc$_3$N@$I_h$-C$_{80}$). This compound has retention time 37.3 min on a Buckyprep column (10 x 250mm) - toluene 2 mL/min.

Figure 3.5 $^1$H-$^{13}$C HMQC spectrum of N-(benzyl-4-diphenylaminophenyl)-[5,6]-Sc$_3$N@$I_h$-C$_{80}$ fulleropyrrolidine
\(^1\)H NMR (500 MHz, CS\(_2/\)CD\(_2\)Cl\(_2\) 4:1, TMS) 7.46 (d, 2H, \(^3\)J\(_{\text{H,H}}\)= 8.5 Hz, ArH), 7.33 (t, 4H, \(^3\)J\(_{\text{H,H}}\)= 7.5 Hz, ArH), 7.20-7.15 (m, 6H, ArH), 7.09 (t, 2H, \(^3\)J\(_{\text{H,H}}\)= 7.5 Hz, ArH), 4.13 (d, 2H, \(^2\)J\(_{\text{H,H}}\)= 10 Hz, N-CH\(_2\)), 3.99 (s, 2H, \(\varphi\)-CH\(_2\)-N), 2.99 (d, 2H, \(^2\)J\(_{\text{H,H}}\)= 10 Hz, N-CH\(_2\)). (See Figure 3.5) MALDI \(m/z\) 1411.68 (negative ionization, 9-nitroanthracene as matrix). The \(^1\)H-\(^{13}\)C HMQC spectrum of compound 18 (See Figure 3.5) shows a correlation between both pyrrolidine protons and a \(^{13}\)C signal at 69.0 ppm; this is clear evidence that the addition occurred at a [5,6] bond on Sc\(3\)N@I\(_h\)-C\(_{80}\). All the protons in the aromatic region are observed as sharp signals indicating that the TPA addend does not have the same dynamic effect observed in the \(^1\)H spectrum of compound 16.

Following the same procedure used in the preparation of compound 18 but using C\(_{60}\) (23.2 mg, 32.2 \(\mu\)mol, 1 eq), N-(benzyl-4-diphenylaminophenyl)glycine (30.2 mg, 95.5 \(\mu\)mol, 3 eq) and paraformaldehyde (24.0 mg, 800 \(\mu\)mol, 25 eq). N-(benzyl-4-diphenylaminophenyl)-[6,6]-C\(_{60}\) fulleropyrrolidine was obtained with a 32% yield (10.6 mg, 10.3 \(\mu\)moles) after purification. \(^1\)H NMR (500 MHz, CS\(_2/\)CD\(_2\)Cl\(_2\) 2:1, TMS) 7.58 (d, 2H, \(^3\)J\(_{\text{H,H}}\)= 8.5 Hz, ArH), 7.27 (t, 4H, \(^3\)J\(_{\text{H,H}}\)= 7.5 Hz, ArH), 7.16 (d, 2H, \(^3\)J\(_{\text{H,H}}\)= 8.5 Hz, ArH), 7.12 (d, 4H, \(^3\)J\(_{\text{H,H}}\)= 7.5 Hz, ArH), 7.02 (t, 2H, \(^3\)J\(_{\text{H,H}}\)= 7.5 Hz, ArH), 4.50 (s, 4H, CH\(_2\)-N), 4.28 (s, 2H, \(\varphi\)-CH\(_2\)-N). \(^{13}\)C NMR (125 MHz, CS\(_2/\)CD\(_2\)Cl\(_2\) 2:1, TMS) 155.14 q, 147.79 q, 147.40 q, 147.33 q, 146.37 q, 146.24 q, 146.18 q, 145.82 q, 145.59 q, 145.40 q, 144.69 q, 143.23 q, 142.76 q, 142.39 q, 142.21 q, 142.03 q, 140.32 q, 136.45 q, 132.21 q, 129.84 CH, 129.48 CH, 124.48 CH, 124.08 CH, 123.08 CH, 70.86 q, 67.83 Bz-N-(CH\(_2\))\(_2\), 58.67 \(\varphi\)-CH\(_2\)-N. (See Figure 3.6) MALDI \(m/z\) 1020.47 (positive ionization, 9-nitroanthracene as matrix).
A comparison of the thermal stability of compounds 16 and 18 was made by preparing a solution of the two compounds in $\alpha$-DCB and heating up the mixture in a flask open to the air and the retro cycloaddition process was followed by HPLC (See Figure 3.7). The 2-substituted derivative (compound 16) decomposes more easily than the $N$-substituted derivative. The retro cycloaddition reaction depends on the attached addends. This behavior is explained by the relative thermodynamic stabilities of the intermediate azomethine ylides formed both during the formation and decomposition of
these compounds. Therefore, the substituent at the 2-position stabilizes the azomethine ylide more efficiently than the $N$-substituted compound.

Figure 3.7 Thermal stability of isomeric TPA-[5,6]-Sc$_3$N@I$_x$C$_{80}$-fulleropyrrolidines. Buckyprep column (10 x 250 mm) eluting with toluene 2.0 mL/min

2.2. Porphyrin based dyads

Synthetic meso-substituted porphyrins have emerged as important building blocks for the construction of fullerene based donor acceptor systems. They are synthetic analogues of the naturally occurring chlorophylls ($\beta$-substituted porphyrins) and can successfully mimic their functions. Substituted porphyrins are relatively easy to prepare and the complexation with different metals or the introduction of different addends in the meso and/or $\beta$ positions provide a wide range or redox behaviors. They have excellent photophysical properties such as high molar extinction coefficients in the visible range and fast energy transfer from their excited states towards neighbor acceptor molecules. On the other hand, the highly conjugated $p$-phenyleneethynylene is known
for its behavior as a molecular wire that facilitates the charge transfer between donor and fullerene acceptor systems connected at the ends because the energies of the C\textsubscript{60} HOMOs match those of \textit{p}-phenyleneethynylene, which facilitates electron/hole injection into the wire.\textsuperscript{181}

Here we report the synthesis and characterization of 3 different donor acceptor systems using Sc\textsubscript{3}N@I\textsubscript{b}-C\textsubscript{80} as the acceptor and a porphyrin as the donor. They were connected via \textit{p}-phenyleneethynylene systems with a [2,2]paracyclophane in the middle in order to modulate the electron conjugation through the bridge. The starting porphyrin [2,2]paracyclophane derivatives were prepared by Professor’s Nazario Martín research group and they were used as received.

2.2.1. Synthesis of 2-AM487-[5,6]-Sc\textsubscript{3}N@I\textsubscript{b}-C\textsubscript{80}

![Figure 3.8 Synthesis of 2-AM487-[5,6]-Sc\textsubscript{3}N@I\textsubscript{b}-C\textsubscript{80}](image-url)
4.6 mg of Sc$_3$N@I$_8$-C$_{80}$ (4.15 µmol, 1 eq), 20.2 mg of AM487-CHO 19 (15.8 µmol, 3.8 eq) and 0.52 mg of sarcosine (5.8 µmol, 1.4 eq) was poured in a 50 mL Schlenk flask under argon. 20 mL of o-dichlorobenzene:DMF 4:1 solvent mixture was added and the stirring started. The reaction mixture was heated to 150°C while monitoring the progress by TLC using silica plates eluting with CS$_2$ to remove the unreacted Sc$_3$N@I$_8$-C$_{80}$ and a second elution with CS$_2$/toluene 1:1 in order to elute the product and part of the unreacted aldehyde (compound 19). Once the formation of bis and poly adducts was detected the reaction mixture was removed from the heat source in order to stop the reaction. The solvent was removed under a stream of nitrogen. The remaining solid was then dissolved in CS$_2$ and purified on a silica gel column eluting first with CS$_2$ to remove the unreacted Sc$_3$N@I$_8$-C$_{80}$ followed by increasing polarity mixtures of CS$_2$ and toluene for eluting the product and to recover the unreacted AM487-CHO aldehyde.

Figure 3.9 MALDI-TOF mass spectrum of 2-AM487-[5,6]-Sc$_3$N@I$_8$-C$_{80}$. Negative ionization mode (9-nitroanthracene as matrix)
The fraction containing the product was further purified by HPLC using a PBB column (4.6 x 250 mm) eluting with toluene at 2.0 mL/min. Compound 20 has a retention time of 16.5 min under those conditions. 1.7 mg of product was obtained (13.6% yield).

Figure 3.10 500 MHz $^1\text{H}$ NMR spectrum of 2-AM-487-[5,6]-Sc$_3$N@I$_y$-C$_{80}$ (aromatic region)

$^1\text{H}$ NMR (500 MHz, CS$_2$/Acetone-d6 external) $\delta$ 9.0 – 8.8 (m, 8H, pyrrolic $\beta$-protons), 8.21 (d, 2H, $^3J_{(H,H)}$ = 8.0 Hz, ArH porphyrin), 8.01 (m, 6H, ArH porphyrin), 7.92 (d, 2H, $^3J_{(H,H)}$ = 8.0 Hz, ArH porphyrin), 7.69 (m, 3H, ArH porphyrin), 7.57 (d, 1H, $^3J_{(H,H)}$ = 15.0 Hz, Vinyl), 7.25 (d, 1H, $^3J_{(H,H)}$ = 15.0 Hz, Vinyl), 7.15 (br, 1H, ArH-
[2,2]paracyclophane), 7.01 (br, 1H, ArH-[2,2]paracyclophane), 6.91 (br, 1H, ArH-[2,2]paracyclophane), 6.56 – 6.47 (m, 3H, ArH-[2,2]paracyclophane), 4.30 (d, 1H, $^2J_{(H,H)}$ = 9.5 Hz, CH$_2$ pyrrolidine), 3.80 – 2.90 (m, 10H, eight from [2,2]paracyclophane CH$_2$ groups a two from the pyrrolidine ring), 3.06 (s, 3H, N-CH$_3$), 1.54 (br, 54H, tBu groups).

MALDI m/z 2411.87 (negative ionization, 9-nitroanthracene as matrix).

2.2.2. Synthesis of 2-AM361-[5,6]-Sc$_3$N@I$_h$-C$_{80}$

![Synthesis of 2-AM361-[5,6]-Sc$_3$N@I$_h$-C$_{80}$](image)

Figure 3.11 Synthesis of 2-AM-361-[5,6]-Sc$_3$N@I$_h$-C$_{80}$

10.0 mg of Sc$_3$N@I$_h$-C$_{80}$ (9.01 µmol, 1 eq), 25.0 mg of aldehyde 21 (13.3 µmol, 1.5 eq) and 0.81 mg of sarcosine (9 µmol, 1 eq) was poured in a 100 mL Schlenk flask under argon. 50 mL of o-dichlorobenzene:DMF 4:1 solvent mixture was added. The reaction
mixture was heated to 150°C while stirring for 15 minutes. The progress of the reaction was followed by TLC using silica plates eluting with CS₂ to remove the unreacted Sc₃N@I₆-C₈₀ and a second elution with pure toluene in order to elute the product and part of the unreacted aldehyde 21.

![NMR Spectrum](image)

Figure 3.12 500 MHz ¹H NMR spectrum of 2-AM361-[5,6]-Sc₃N@I₆-C₈₀ (aromatic region)

The solvent was removed overnight under a stream of nitrogen. The remaining solid was then dissolved in CS₂ and purified on a silica gel column eluting first with CS₂ for removing the unreacted Sc₃N@I₆-C₈₀ followed by increasing polarity mixtures of CS₂
and toluene for eluting the product and to recover the unreacted aldehyde 21. The fraction containing the product was further purified by HPLC using a PBB column (4.6 x 250 mm) eluting with toluene at 2.0 mL/min. Compound 22 has a retention time of 9.6 min under those conditions. After evaporating the toluene and washing the remaining solid with diethyl ether, 3.2 mg of product was obtained. (11.8% yield).

Figure 3.13 (a) 500 MHz $^1$H NMR spectrum of 2-AM361-[5,6]-Sc$_3$N@I$_8$C$_{80}$ (aliphatic region) (b) Selective TOCSY experiment showing the signals of the n-hexyl aliphatic chains.
1H NMR (500 MHz, CS$_2$/Acetone-d6 external) $\delta$ 9.1-8.95 (m, 8H, pyrrolic $\beta$-protons), 8.27 (d, 2H, $^3J_{(H,H)} =$ 7.5 Hz, ArH porphyrin), 8.16 (m, 6H, ArH porphyrin), 8.00 (d, 2H, $^3J_{(H,H)} =$ 7.5 Hz, ArH porphyrin), 7.88 (m, 3H, ArH porphyrin), 7.65 – 6.4 (m, 16H, Vinyl and/or ArH in the bridge), 4.40 - 4.20 (m, 9H, eight from O-CH$_2$ and one from the pyrrolidine ring), 4.00 - 3.00 (m, 10H, eight from [2,2]paracyclophane CH$_2$ groups a two from the pyrrolidine ring), 2.6 (s, 3H, N-CH$_3$), 2.03 (m, 8H, -CH$_2$-), 1.70 (m, 8H, -CH$_2$-), 1.60 (m, 54H, tBu groups), 1.50 (m, 16H, -CH$_2$-), 1.10 (m, 12H, -CH$_3$). MALDI m/z 3013.02 (negative ionization, 9-nitroanthracene as matrix).

2.2.3. Synthesis of 2-AM362-[5,6]-Sc$_3$N@I$_{8r}$-C$_{80}$

![Synthesis of 2-AM362-[5,6]-Sc$_3$N@I$_{8r}$-C$_{80}$](image)

Figure 3.14 Synthesis of 2-AM362-[5,6]-Sc$_3$N@I$_{8r}$-C$_{80}$
8.6 mg of Sc$_3$N@I$_h$-C$_{80}$ (7.75 µmol, 1 eq), 20.0 mg of aldehyde 23 (9.59 µmol, 1.23 eq) and 0.70 mg of sarcosine (7.8 µmol, 1 eq) was poured in a 50 mL Schlenk flask under argon. 25 mL of o-dichlorobenzene:DMF 4:1 solvent mixture was added. The reaction mixture was heated to 150°C while stirring for 3 hours. The progress of the reaction was followed by TLC using silica plates eluting with CS$_2$ to remove the unreacted Sc$_3$N@I$_h$-C$_{80}$ and a second elution with pure toluene in order to elute the product and the unreacted aldehyde 23.

Figure 3.15 500 MHz $^1$H NMR spectrum of 2-AM362-[5,6]-Sc$_3$N@I$_h$-C$_{80}$ (aromatic region)
After evaporating the solvent, the remaining solid was then dissolved in CS$_2$ and purified on a silica gel column eluting first with CS$_2$ for removing the unreacted Sc$_3$N@I$_{p}$-C$_{80}$ followed by increasing polarity mixtures of CS$_2$ and toluene for eluting the product and to recover the unreacted aldehyde 23. The fraction containing the product was further purified by HPLC using a PBB column (4.6 x 250 mm) eluting with toluene at 2.0 mL/min. Compound 24 has a retention time of 11.4 min under those conditions. After evaporating the toluene and washing the remaining solid with diethyl ether, 2.5 mg of product was obtained. (10.0 % yield).

Figure 3.16 $^1$H-$^{13}$C HSQC experiment of 2-AM362-[5,6]-Sc$_3$N@I$_{p}$-C$_{80}$ (aliphatic region)
\(^1\)H NMR (500 MHz, CS\(_2\)/Acetone-d6 external) \(\delta\) 8.98 (m, 8H, pyrrolic \(\beta\)-protons), 8.21 (d, 2H, \(^3\)J\(_{(H,H)}\) = 7.5 Hz, ArH porphyrin), 8.10 (m, 6H, ArH porphyrin), 7.95 (d, 2H, \(^3\)J\(_{(H,H)}\) = 7.5 Hz, ArH porphyrin), 7.82 (m, 3H, ArH porphyrin), 7.70 – 7.40 (m, 10H, Vinyl and/or ArH in the bridge), 7.39 – 7.00 (m, 12H, Vinyl and/or ArH in the bridge), 6.8 (br, 4H, Vinyl and/or ArH in the bridge), 6.42 (m, 2H, Vinyl and/or ArH in the bridge), 4.20 - 4.00 (m, 9H, eight from O-CH\(_2\) and one from the pyrrolidine ring), 3.70 – 2.80 (m, 10H, eight from [2,2]paracyclophane CH\(_2\) groups a two from the pyrrolidine ring), 2.49 (s, 3H, N-CH\(_3\)), 1.93 (m, 8H, -CH\(_2\)-), 1.62 (m, 8H, -CH\(_2\)-), 1.54 (m, 54H, tBu groups), 1.40 (m, 16H, -CH\(_2\)-), 1.07 (m, 12H, -CH\(_3\)). MALDI \(m/z\) 3221.04 (negative ionization, 9-nitroanthracene as matrix).

Figure 3.17 MALDI-TOF mass spectrum of 2-AM362-[5,6]-Sc\(_5\)N@I\(_{11}\)-C\(_{60}\) (Negative ionization mode – 9-nitroanthracene as matrix)
3. Electrochemical properties

The electrochemical properties of the triphenylamine dyads 16 and 18 were studied by cyclic voltammetry (CV) and Osteryoung Square Wave Voltammetry (OSWV) experiments. Their redox potentials were compared to those of their C₆₀ analogues, C₆₀, Sc₃N@I₆-C₈₀ and 4-(diphenylamino) benzyl alcohol as references. All the redox potentials are collected in Table 3.1. As observed in Figure 3.18 traces b and c, both compound 16 and 18 have three reversible reductions, typical for a [5,6]-Sc₃N@I₆-C₈₀ fulleropyrrolidines.²⁸ In the anodic scan, compound 16 displays two irreversible oxidation processes; the first process is probably related to the oxidation of the triphenylamine,¹⁷⁵ but also may be the result of a pyrrolidine based oxidation.⁴³

Table 3.1 Redox potentials of triphenylamine based dyads. All the values are reported in volts vs the Fe/Fe⁺ redox pair. Supporting electrolyte nBu₄NPF₆ 0.050 M in o-DCB. Scan rate 100 mV/s, glassy carbon working electrode, Pt counter, Ag wire as reference.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cage Based</th>
<th>Addend Based</th>
<th>Cage Based</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E⁺/⁺²</td>
<td>E₀/⁺</td>
<td>E₀/+</td>
</tr>
<tr>
<td>C₆₀</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sc₃N@I₆-C₈₀</td>
<td>+1.09</td>
<td>+0.59</td>
<td>-</td>
</tr>
<tr>
<td>Compound 16</td>
<td>+1.06</td>
<td>-</td>
<td>+0.39</td>
</tr>
<tr>
<td>Compound 18</td>
<td>+0.99</td>
<td>+0.63</td>
<td>+0.32</td>
</tr>
<tr>
<td>2-TPA-C₆₀</td>
<td>-</td>
<td>-</td>
<td>+0.56</td>
</tr>
<tr>
<td>N-TPA-C₆₀</td>
<td>-</td>
<td>-</td>
<td>+0.55</td>
</tr>
<tr>
<td>4-(diphenylamino) benzyl alcohol</td>
<td>-</td>
<td>-</td>
<td>+0.51</td>
</tr>
</tbody>
</table>
The second oxidation process is centered on the fullerene cage. In the case of compound 18 three irreversible processes are observed. The first oxidation process at +0.32 V is related to either the oxidation of the triphenylamine group\textsuperscript{175} or the pyrrolidine\textsuperscript{43} and the other processes at +0.63 V and +0.99 V correspond to the oxidation of the fullerene cage.

Figure 3.18 Electrochemical studies of TPA-Sc$_3$N@I$_n$-C$_{60}$ fulleropyrrolidine dyads. Left – Cyclic voltammograms of (a) Sc$_3$N@I$_n$-C$_{60}$ (b) 2-TPA-Sc (Compound 16) (c) N-TPA-Sc (Compound 18) Right - Osteryoung Square Wave Voltammetry (OSWV) of (d) Sc$_3$N@I$_n$-C$_{60}$ (d) 2-TPA-Sc (Compound 16) (f) N-TPA-Sc (Compound 18)

For the C$_{60}$ compounds, three equally spaced reversible reductions are observed. They are cathodically shifted 110 and 180 mV, respectively, when compared to pristine C$_{60}$ (See Figure 3.19). In the anodic scan an irreversible oxidative process occurs and it is related to the oxidation of the TPA addend,\textsuperscript{175} an it leads to the formation of a polymer film that starts growing on the working electrode. This film formation was observed for
both the Sc₃N@I₆-C₈₀ and C₆₀ dyads and it was further investigated in more detail (See chapter 5).

Figure 3.19 Cyclic voltammograms of triphenylamine C₆₀ dyads. (a) C₆₀ (b) N-TPA-C₆₀ (c) 2-TPA-C₆₀ (d) 4-(diphenylamino)benzyl alcohol

The reductive electrochemical behavior of the porphyrin based dyads 20, 22 and 24 (See Figure 3.20, Figure 3.21 and Figure 3.22) displays not only the three typical reduction processes observed for the [5,6]-Sc₃N@I₆-C₈₀ fulleropyrrolidines, but also two extra reduction processes that are porphyrin based.¹⁸² The first reduction of the porphyrin is observed at -2.0 V vs Fc/Fc⁺ whereas the second process is overlapped with the third reduction of the fullerene cage at -2.30 V.
Table 3.2 Redox potentials of porphyrin based dyads. All the values are reported in volts vs the Fc/Fc\(^+\) redox pair. The supporting electrolyte was \(n\text{Bu}_4\text{NPF}_6\) 0.050 M in \(\sigma\text{-DCB}\). Scan rate 100 mV/s, glassy carbon working electrode, Pt counter, Ag wire as reference.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Addend and/or cage oxidations</th>
<th>Cage reductions</th>
<th>Cage and/or addend reductions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc(<em>3)N@(I_6)-C(</em>{80}) (^{20})</td>
<td>+1.09 +0.59</td>
<td>-</td>
<td>-1.26 -1.62</td>
</tr>
<tr>
<td>Compound 19</td>
<td>+1.01 +0.63</td>
<td>- +0.37</td>
<td>-</td>
</tr>
<tr>
<td>Compound 20</td>
<td>+1.08 +0.60</td>
<td>- +0.29</td>
<td>-1.16 -1.54</td>
</tr>
<tr>
<td>Compound 21</td>
<td>+0.87 +0.67 +0.54 +0.38</td>
<td>- -</td>
<td>-2.00 -2.25</td>
</tr>
<tr>
<td>Compound 22</td>
<td>+0.84 +0.57 +0.44 +0.25</td>
<td>-1.22 -1.62</td>
<td>- -2.00 -2.32</td>
</tr>
<tr>
<td>Compound 23</td>
<td>+1.02 +0.70 +0.52 +0.37</td>
<td>- -</td>
<td>-2.00 -2.25</td>
</tr>
<tr>
<td>Compound 24</td>
<td>+0.80 +0.55 +0.40 +0.28</td>
<td>-1.18 -1.56</td>
<td>-1.98 -2.27</td>
</tr>
</tbody>
</table>

Figure 3.20 Electrochemical studies of AM-487 dyad. Left – Cyclic voltammograms of (a) Sc\(_3\)N@\(I_6\)-C\(_{80}\) (b) AM487-CHO (Compound 19) (c) Compound 20 Right – Osteryoung Square Wave Voltammetry (OSWV) of (d) Sc\(_3\)N@\(I_6\)-C\(_{80}\) (e) AM487-CHO (Compound 19) (f) Compound 20
Figure 3.21 Electrochemical studies of AM-361 dyad. Left – Cyclic voltammograms of (a) Sc\textsubscript{3}N@I\textsubscript{r-C\textsubscript{80}} (b) AM361-CHO (Compound 21) (c) Compound 22 Right - Osteryoung Square Wave Voltammetry (OSWV) of (d) Sc\textsubscript{3}N@I\textsubscript{r-C\textsubscript{80}} (e) AM361-CHO (Compound 21) (f) Compound 22

Figure 3.22 Electrochemical studies of AM-362 dyad. Left – Cyclic voltammograms of (a) Sc\textsubscript{3}N@I\textsubscript{r-C\textsubscript{80}} (b) AM362-CHO (Compound 23) (c) Compound 24 Right - Osteryoung Square Wave Voltammetry (OSWV) of (d) Sc\textsubscript{3}N@I\textsubscript{r-C\textsubscript{80}} (e) AM362-CHO (Compound 23) (f) Compound 24
The anodic scan is more complex because the starting aldehydes (compounds 19, 21 and 23) have three, four and five oxidation processes, respectively. That oxidative behavior is also observed for the dyads (compounds 20, 22 and 24), in addition to the oxidation processes occurring on the fullerene cage and the pyrrolidine ring. For compound 20 this oxidative process is observed as a shoulder on the OSWV anodic scan at +0.23V, in compound 22 the pyrrolidine oxidation process is not observed clearly probably because it overlaps with the first oxidation of the porphyrin. For compound 24 the oxidative pyrrolidine oxidation is clearly observed at +0.28 V.
4. Conclusions and Recommendations

The preparation of two isomeric donor acceptor systems incorporating triphenylamine was achieved. It was observed that the N-substituted compound is more stable thermally than the 2-substituted one. Photophysical studies conducted by Professor’s Guldi research group revealed that both compounds produce charge separated states upon light irradiation with lifetimes of 2200 pS for dyad 16 and 3000 pS for compound 18. These values are considerably higher than those of their C₆₀ analogues (155 and 505 pS, respectively). These results evidence the advantage of using Sc₃N@I₈-C₈₀ to substitute C₆₀ in the preparation of donor acceptor systems.

The preparation of three different donor acceptor systems using a porphyrin as donor and connected to Sc₃N@I₈-C₈₀ with a molecular wire was achieved. The photochemical studies conducted by Professor’s Guldi research group revealed that compound 22 forms a charge separated state with a lifetime of 3.2 µS. Compound 24 exhibits a charge separated state with a lifetime of 2.6 µS. These are the longest lived charge separated states that incorporate endohedral metallo fullerenes.

The preparation of donor acceptor systems with a different connection strategy than the 1,3-dipolar cycloadditions⁴³,¹⁵¹ should be made in order to avoid the undesirable retro cycloaddition reaction that causes the decomposition of the dyads.
CHAPTER FOUR
PREPARATION OF BINGEL HIRSCH DERIVATIVES OF
M$_3$N@I$_h$-C$_{80}$ (M=Lu, Sc, Y)

1. Introduction

![Diagram showing the relationship between orbitals energy difference and open circuit voltage]

Figure 4.1 Correlation between the orbitals energy difference between donor and acceptor and the open circuit voltage in organic solar cells

The open circuit voltage in organic solar cells correlates linearly with the energy difference between the HOMO of the donor and the LUMO of the acceptor (See Figure 4.1)\textsuperscript{153} and the overall efficiency of a solar cell is defined by:

$$\eta = (V_{OC} * I_{SC} * FF) / P_{IN}$$

Where $V_{OC}$ is the open circuit voltage, $I_{SC}$ is the short circuit current, FF is the filling factor and $P_{IN}$ is the power of the incident light. The open circuit voltage is then directly related to the efficiency of any solar cell. It has been estimated that increasing the LUMO energy level of the electron acceptor by ~600 mV compared to PCBM could in principle double the efficiency of organic solar cells if the other parameters remain constant.\textsuperscript{183}
Considering the reduction potential of Lu$_3$N@I$_h$-C$_{80}$, finding new methods for its functionalization and tuning the electrochemical properties of its derivatives is particularly important; not only because it is one of the most abundant TNT-EMFs but also because its electrochemical properties make it the ideal candidate for the preparation of materials for the construction of organic solar cells.$^{67,122}$

The Bingel-Hirsch reaction$^{49,50,54}$ is one of the most popular methods used for the chemical functionalization of fullerenes. Its use is much extended due to the easy accessibility of the malonic acid derivatives. This reaction was successfully applied for the functionalization of Y$_3$N@I$_h$-C$_{80}$ and Er$_3$N@I$_h$-C$_{80}$ but failed on Sc$_3$N@I$_h$-C$_{80}$.$^{27}$ The difference in the reactivity was attributed to the encapsulated trimetallic cluster.$^{27}$ The Bingel-Hirsch reaction on empty cage fullerenes, produces cyclopropanated derivatives, but in the case of Y$_3$N@I$_h$-C$_{80}$ it produces an open cage fullerene or “fulleroid” due to the norcaradiene rearrangement (See Figure 4.2).$^{51}$ Contrary to what occurs with the cyclopropanated empty cage fullerenes these structures are stable under reductive conditions; which makes them particularly useful because donor-acceptor dyads must tolerate both the oxidation of the donor and the reduction of the acceptor.

![Figure 4.2 Mechanism for the formation of open cage fullerene derivatives (fulleroids) (a) cyclopronation (b) Norcaradiene rearrangement$^{51}$](image)
A recent report showed that the Bingel-Hirsch derivatives of both Sc$_3$N@I$_{h}$-C$_{80}$ and Lu$_3$N@I$_{h}$-C$_{80}$ can be prepared by refluxing TNT-EMFs in chlorobenzene with diethylmalonate in the presence of Mn(III) acetate dehydrate.$^{52}$ This reaction proceeds through a free radical mechanism and produces poly adducts with up to 8 addends for Sc$_3$N@I$_{h}$-C$_{80}$ and 10 addends in the case of Lu$_3$N@I$_{h}$-C$_{80}$. The poly additions become hard to control and those reaction conditions are not compatible with several substrates.

Here we report the development of a new protocol for the preparation of Bingel-Hirsch adducts in high yield for both Sc$_3$N@I$_{h}$-C$_{80}$ and Lu$_3$N@I$_{h}$-C$_{80}$ under more typical conditions, using dimethyl formamide (DMF) in the reaction solvent mixture. The presence of DMF has made it possible to prepare these adducts routinely and in reasonably high yields without the need to generate the intermediate radicals. The electrochemical properties of the obtained derivatives were studied and we observed that different addends produce different effects on the reduction potentials of the prepared compounds. Part of the experimental procedures and graphs presented here are a pre-peer reviewed version of the following article (See Appendix B for the copyright letter):

2. Synthesis of the compounds

Preliminary essays involved the reaction of $\text{Sc}_3\text{N} @ I_h$-$\text{C}_{80}$ with $n$-$\text{BuLi}$ in toluene solution. A clear change in the color of the solution was observed followed by precipitation of what presumably corresponds to insoluble lithium salts of $\text{Sc}_3\text{N} @ I_h$-$\text{C}_{80}$ because the $^7\text{Li}$ NMR signal of $n$-$\text{BuLi}$ (See Figure 4.3) disappeared after the reaction with $\text{Sc}_3\text{N} @ I_h$-$\text{C}_{80}$. Quenching of this reaction mixture with 1-bromobutane failed to produce isolable products. However, when the reaction mixture was quenched with a 9-bromofluorene a mass corresponding to the addition of one fluorene unit to $\text{Sc}_3\text{N} @ I_h$-$\text{C}_{80}$ was observed; this result encouraged us to further explorations until we found optimal conditions to run the Bingel-Hirsch reaction on both $\text{Sc}_3\text{N} @ I_h$-$\text{C}_{80}$ and $\text{Lu}_3\text{N} @ I_h$-$\text{C}_{80}$.

Figure 4.3 194 MHz $^7\text{Li}$ NMR spectrum of $n$-$\text{BuLi}$ in toluene.
2.1. Synthesis of 9,9’-((6,6)-Sc$_3$N@I$_{h}$-C$_{80}$)-spirofluorene

Figure 4.4 Synthesis of 9,9’-((6,6)-Sc$_3$N@I$_{h}$-C$_{80}$)-spirofluorene

In a 50 mL Schlenk flask equipped with a magnetic stirring bar was poured Sc$_3$N@I$_{h}$-C$_{80}$ (2.04 mg, 1.83 µmol, 1 eq) and 9-bromofluorene (1.55 mg, 6.32 µmol, 3.4 eq). 10 mL of o-DCB were added and stirring was started while keeping the reaction mixture under argon. By using a 10 µL HPLC syringe, 1 drop of DBU was added and the whole mixture was stirred overnight at room temperature. Then the reaction mixture was quenched with 100 µL of glacial acetic acid. The solvent was evaporated under a nitrogen stream and the solid residue re-dissolved in CS$_2$ and filtered through a 1 cm silica plug. The CS$_2$ was evaporated and the residual solid washed with diethyl ether. Finally the solid was re-dissolved in toluene, filtered and separated by HPLC using a Buckyprep column (10 x 250 mm) eluting with toluene 2 mL/min. Compound 25 has a retention time of 66.8 min (See Figure 4.5). $^1$H NMR (500 MHz, CS$_2$/CDCl$_3$ 4:1, TMS): δ 8.68 (dd, 2H, $^3$J$_{(H,H)}$=8.2 Hz, $^4$J$_{(H,H)}$=0.8 Hz; CHs H1,H1’), 7.91 (dd, 2H, $^3$J$_{(H,H)}$=7.3 Hz, $^4$J$_{(H,H)}$=0.8 Hz; CHs H4,H4’), 7.53 (dd, 2H, $^3$J$_{(H,H)}$=7.3 Hz, $^4$J$_{(H,H)}$=0.8 Hz; CHs H3,H3’), 7.40 (dd, 2H, $^3$J$_{(H,H)}$=7.4 Hz, $^4$J$_{(H,H)}$=8.2 Hz, $^4$J$_{(H,H)}$=0.8 Hz; CHs H2,H2’); MALDI-TOF (negative ionization mode 9-nitroanthracene as matrix): m/z: 1274.90
Figure 4.5 HPLC separation of compound 25. Buckyprep column (10 x 250 mm) – toluene 2 mL/min

Figure 4.6 500 MHz $^1$H NMR spectrum of compound 25

The $^1$H NMR spectrum of compound 25 (See Figure 4.6) shows a single set of signals consistent with the reaction occurring on a [6,6] bond. The resonance of the protons at the 1 and 1’ positions are downfield shifted by ~1.0 ppm when compared to 9-bromofluorene. That occurs because the rigid structure of compound 25 keeps those
hydrogen atoms close to the fullerene cage so they are affected by the ring currents on the surface of the fullerene cage.\textsuperscript{184}

Figure 4.7 MALDI-TOF mass spectrum of compound 25. Negative ionization mode (9-nitroanthracene as matrix)

2.2. Synthesis of 81-di(ethoxycarbonyl)-1,2-methano-[6,6]-Sc\textsubscript{3}N@I\textsubscript{h}-C\textsubscript{80} fullerene

Figure 4.8 Synthesis of 81-[di(ethoxycarbonyl)-1,2-methano-[6,6]-Sc\textsubscript{3}N@I\textsubscript{h}-C\textsubscript{80}] fullerene
Sc$_3$N@$_n$-$\text{C}_{80}$ (6.9 mg, 6.22 µmol, 1 eq) and 10.0 mg of NaH 60% oil suspension were charged into a 50 mL Schlenk flask and poured under argon. 8.0 mL of o-DCB and 2.0 mL of dimethylformamide (DMF) were added and stirring was started. A solution of 2-bromodiethylmalonate (4.0 µL, 5.68 mg, 23.7 µmol, 3.8 eq) dissolved in 2.0 mL of toluene was added dropwise. The reaction mixture was then heated to 60°C and monitored using TLC (First eluting with CS$_2$, followed by CS$_2$/CH$_2$Cl$_2$ 2:1). After stirring for 20 minutes and when the formation of bis-adducts was evident on the TLC plates, glacial acetic acid was added until the bubbling ceased. The solvent was evaporated under a nitrogen stream and the solid residue dissolved in toluene and the reaction mixture separated by HPLC on a PBB column (4.6 x 250 mm) eluting with toluene/o-DCB 5% at a flow rate of 2 mL/min. The retention time was 13.5 min (3.2 mg, 40.5% yield).

Figure 4.9  HPLC separation of products of the Bingel-Hirsch reaction between Sc$_3$N@$_n$-$\text{C}_{80}$ and diethylmalonate. (a) Reaction mixture (b) Compound 27 (c) Compound 26 (d) Compound 28 (e) polyadducts fraction
Compound 26 $^1$H NMR (500 MHz, CS$_2$/CD$_2$Cl$_2$ 4:1, TMS): $\delta$ 4.89 (q, 4H, $^3J_{(H,H)}$=7.0 Hz, -COO-CH$_2$), 1.43 (t, 6H, $^3J_{(H,H)}$=7.0 Hz, -CH$_3$). MALDI-TOF (positive ionization mode 9-nitroanthracene as matrix): $m/z$: 1267.94

Figure 4.10 500 MHz $^1$H NMR spectrum of compound 26

The $^1$H NMR spectrum of compounds 26 (See Figure 4.10) and 27 agree completely with the previous reported values.$^{52}$ There is only one set of signals confirming that the addition occurred on a [6,6] bond of the Sc$_3$N@I$_h$-C$_{80}$. The formation of compounds 27 and 28 may be the result of the hydrolysis reactions of the malonate groups. However, when NaH is replaced by DBU the reaction hardly proceeds even after days; most of the
Sc$_3$N@I$_r$-C$_{80}$ actually precipitates out of the solution presumably after forming a charge transfer complex. An EPR spectrum of the reaction mixture did not show any signal, thus more than one electron may be involved in the process. That behavior is typical and it is used for the large scale separation of C$_{60}$ from higher fullerenes by precipitation of the latter with DBU.$^{185}$ The complexation process can be inhibited by increasing the temperature or by increasing the polarity of the solvent. There is a problem with the second approach because Sc$_3$N@I$_r$-C$_{80}$ is not soluble in polar solvents. Thus a 4:1 mixture of o-DCB/ DMF is a good balance that allows increasing the polarity of the solvent mixture while providing a medium capable of dissolving Sc$_3$N@I$_r$-C$_{80}$. Theoretical studies have revealed that the first step during the Bingel-Hirsch reaction is an exothermic barrierless process, but the activation energy for the elimination step is strongly affected by the polarity of the solvent.$^{186}$ Polar solvents lower the activation energy of the intermediate transition state; thus the presence of DMF can help by lowering the energy barrier of the second step.

Figure 4.11 MALDI-TOF mass spectra of the products of the Bingel-Hirsch reaction between Sc$_3$N@I$_r$-C$_{80}$ and diethyl malonate (a) Compound 27 (b) Compound 28 (c) bis-adducts fraction
2.3. 81-[di(pyrrolidine-$N$-carbonyl)-1,2-methano-[6,6]-Sc$_3$N@$I_p$-$C_{80}$]fullerene

![Chemical reaction](image)

Figure 4.12 Synthesis of 81-[di(pyrrolidine-$N$-carbonyl)-1,2-methano-[6,6]-Sc$_3$N@$I_p$-$C_{80}$]fullerene

Sc$_3$N@$I_p$-$C_{80}$ (2.0 mg, 1.80 µmol, 1 eq), 2-bromo-1,3-dipyrrolidin-1-ylpropane-1,3-dionate$^{187,188}$ (6.0 mg, 16.3 µmol, 9.0 eq) and 30.0 mg of NaH 60% oil suspension were charged into a 50 mL Schlenk flask and poured under argon. 4.0 mL of $o$-DCB and 1.0 mL of dimethylformamide were added and stirring was started. The reaction mixture was then heated to 60 °C and monitored using TLC (first eluting with CS$_2$, followed by CH$_2$Cl$_2$/ethyl acetate/triethanolamine 7:2:1). After stirring for 20 minutes, and when the formation of bis-adducts was evident on the TLC plates, the reaction mixture was cooled and glacial acetic acid was added until the bubbling ceased. The solvent was evaporated under a nitrogen stream and the solid residue dissolved in CS$_2$ and separated on a silica gel column. CS$_2$ was used for eluting the unreacted Sc$_3$N@$I_p$-$C_{80}$ followed by a CH$_2$Cl$_2$/Ethyl acetate/Triethanolamine 7:2:1 mixture for eluting the product (1.2 mg, 54% yield). The retention time on a Buckyprep column (10 x 250 mm) eluting with toluene at 2 mL/min is 28.6 min. $^1$H NMR (500 MHz, CS$_2$/CDCl$_3$ 9:1, TMS): $\delta$ 4.33 (1H, N-CH$_2$-), 4.17 (1H, N-CH$_2$-), 4.00 (1H, N-CH$_2$-), 3.76 (3H, N-CH$_2$-), 3.67 (1H, N-CH$_2$-), 3.56 (1H,
N-CH₂-), 2.02 (8H, N-C-CH₂); MALDI-TOF (negative ionization mode 9-nitroanthracene as matrix): m/z: 1318.01

Figure 4.13 500 MHz ¹H NMR spectrum of compound 29

The signals of the protons in the pyrrolidine rings of compound 29 are broad and have a complex pattern (See Figure 4.13). The lack of equivalency is due to the hindered rotation of the five membered rings combined with the resonance effects resulting from the amide groups.
2.4. Synthesis of 81-[di(pyrrolidine-N-carbonyl)-1,2-methano-[6,6]-Lu₃N@I₆-
C₈₀]fullerene

Lu₃N@I₆-C₈₀ (1.66 mg, 1.11 µmol, 1 eq), 2-bromo-1,3-dipyrrolidin-1-ylpropane-1,3-
dionate¹⁸⁷,¹⁸⁸ (1.8 mg, 6.24 µmol, 5.6 eq) and 10.0 mg, 0.42 mmol of NaH 60% oil
suspension were charged into a 50 mL Schlenk flask and poured under argon. 4.0 mL of
o-DCB and 1.0 mL of dimethylformamide were added and stirring was started. The reaction mixture was then heated to 60 °C and monitored using TLC (first eluting with CS₂, followed by CH₂Cl₂/ethyl acetate/triethanolamine 7:2:1). The reaction was removed from the heating bath once the formation of bis adducts was evident on the TLC plates, then it was quenched with acetic acid. The solvent was evaporated under a nitrogen stream and the solid residue dissolved in CS₂ and separated on a silica gel column. CS₂ was used for eluting the unreacted Lu₃N@I₆-C₈₀ followed by a CH₂Cl₂/ethyl acetate/triethanolamine 7:2:1 mixture for eluting the product. (1.1 mg, 58% yield). The retention time on a PBB column (4.6 x 250 mm) eluting with toluene/o-DCB 5% at 2 mL/min is 19.4 min. ¹H NMR (500 MHz, CS₂/CD₂Cl₂ 4:1, TMS): δ 4.37 (1H, N-CH₂-), 4.22 (1H, N-CH₂-), 4.07 (1H, N-CH₂-), 3.80 (3H, N-CH₂-), 3.69 (2H, N-CH₂-), 2.08 (8H, N-C-CH₂); MALDI-TOF (negative ionization mode 9-nitroanthracene as matrix): m/z: 1708.12

Figure 4.16  HPLC trace of compound 30. PBB column (4.6 x 250 mm) - toluene/o-DCB 95:5, 2 mL/min.
Figure 4.17 500 MHz $^1$H NMR spectrum of compound 30

Figure 4.18 MALDI-TOF mass spectrum of compound 30
The $^1$H NMR spectrum of compound 30 (See Figure 4.17) has the same pattern observed for compound 29. Compared to Sc$_3$N@$I_h$-C$_{80}$ the reaction with Lu$_3$N@$I_h$-C$_{80}$ was slower under the same conditions but the result was the same. The high intensity of the molecular peak in the MALDI-TOF mass spectrum is remarkable considering the difficulty of obtaining mass spectra for TNT-EMF derivatives without fragmentation. Usually TNT-EMF derivatives that do not suffer fragmentation in the MALDI-TOF spectrometer are very robust and do not decompose under typical laboratory conditions.

2.5. Synthesis of 81-[di(ethoxycarbonyl)-1,2-methano-[6,6]-Lu$_3$N@$I_h$-C$_{80}$]fullerene

![Figure 4.19 Synthesis of 81-[di(ethoxycarbonyl)-1,2-methano-[6,6]-Lu$_3$N@$I_h$-C$_{80}$]fullerene](image)

Lu$_3$N@$I_h$-C$_{80}$ (1.80 mg, 1.20 µmol, 1 eq) was poured in a Schlenk flask under argon. 4.0 mL of dry o-DCB and 1.0 mL of DMF were added and the material dissolved. 10 µL of 2-bromodiethyl malonate were added, then by using a 10 µL HPLC syringe 1 drop of
DBU was added, after 1 hour an extra drop of DBU was added and the reaction mixture stirred overnight at room temperature. The reaction was quenched with 2 drops of glacial acetic acid, the solvent removed under a nitrogen stream and the remaining solid dissolved with CS₂ and acetone to help dissolve the black sticky material that was formed. The solution was filtered through a silica plug and the solvent evaporated again. The solid was dissolved in toluene and separated by HPLC on a PBB column (4.6 x 250 mm) eluting with toluene/o-DCB 95:5 at a flow rate of 2 mL/min. Retention time 14.2 min (0.8 mg, 40.0% yield). ^1H NMR (500 MHz, CS₂/CD₂Cl₂ 4:1, TMS): δ 4.64 (q, 4H, ^3J_{(H,H)}=7.0 Hz, -COO-CH₂-), 1.56 (t, 6H, ^3J_{(H,H)}=7.0 Hz, -CH₃). MALDI-TOF (positive ionization mode 9-nitroantracene as matrix): m/z: 1656.80

Figure 4.20 HPLC separation of the products of the Bingel-Hirsch reaction between Sc₃N@I₅-C₈₀ and diethylmalonate. (a) Reaction mixture (b) Compound 32 (c) Compound 31 (d) Compound 33

The HPLC trace of the Bingel-Hirsch reaction of Lu₃N@I₅-C₈₀ is similar to that of Sc₃N@I₅-C₈₀ because the products are similar. The interaction with the stationary phase is barely affected by the encapsulated cluster thus it can be assumed that the products of
this reaction are analogues to those of Sc$_3$N@I$_h$-C$_{80}$. The structure of the main product was confirmed by $^1$H NMR (See Figure 4.21).

Figure 4.21 500 MHz $^1$H COSY NMR spectrum of compound 31

2.6. Synthesis of diethylmalonate-[6,6]-Y$_3$N@I$_h$-C$_{80}$ poly adducts

Figure 4.22 Synthesis of diethylmalonate-[6,6]-Y$_3$N@I$_h$-C$_{80}$ poly adducts
The crystal structures of $M_3N@I_h$-C$_{80}$ ($M = \text{Sc, Lu, Gd}$)$^{1,13,189}$ show that the metal atoms in the cluster have a preference to stay close to either a [5,6] bonds in the case of Sc and close to [6,6] bonds for the bigger metals. However, the metal atoms do not have a fixed position inside the fullerene cage.$^6$ The crystal structure of the diethylmalonate Bingel-Hirsch derivative of $Y_3N@I_h$-C$_{80}$$^{27}$ is in sharp contrast with these observations; because it shows that one of the metal atoms has a strong preference to localize close to the seven membered rings created after the norcaradiene rearrangement.$^{51}$ So we decided to explore whether or not this fixed metal would help to control the addition of the second group to the $I_h$-C$_{80}$ cage.

5.76 mg of $Y_3N@I_h$-C$_{80}$ (4.64 µmol, 1 eq) was poured in a 100 mL Schlenk flask under argon and dissolved with 20 mL of o-DCB. A large excess of 2-bromodiethyl malonate (30 µL, 42.6 mg, 178.19 µmol, 38 eq) was added and DBU (25 µL, 25.45 mg, 167.17 µmol, 36 eq) dissolved in 2 mL of o-DCB was added dropwise during a 4 hours period. The progress of the reaction was followed by HPLC using a Buckyclutcher column (10 x 250 mm) eluting with toluene at 4 mL/min (See Figure 4.23). Since the monoadduct was the dominant fraction, the reaction was allowed to continue overnight. When the monoadduct fraction almost disappeared the solvent was evaporated under a stream of nitrogen. Acetone was added to the sticky residue in order to remove the soluble contaminants and the fullerene derivatives were recovered by filtration of the resulting suspension using an inline Teflon HPLC syringe filter (0.2 µm pore size). The derivatives were recovered from the filter by dissolving them with HPLC grade toluene and separated by preparative TLC (silica plates eluting with CH$_2$Cl$_2$) (See Figure 4.24).
Figure 4.23 Bingel-Hirsch reaction $Y_3 N@I_6 C_{80}$ and 2-bromodiethyl malonate followed by HPLC. Buckyclutcher column (10 x 250 mm) – toluene 4 mL/min

Figure 4.24 Preparative TLC separation of Bingel-Hirsch adducts of $Y_3 N@I_6 C_{80}$ (a) bis adducts (b) tris adducts fraction – Silica gel plate CH$_2$Cl$_2$ mobile phase
The reaction mixture was also analyzed by HPLC (See Figure 4.25). Every fraction in both the TLC plate and the HPLC column was analyzed by MALDI-TOF mass spectroscopy to determine their composition.

![Image](image1.png)

Figure 4.25 HPLC trace of the final reaction mixture between Y₃N@I₆-C₈₀ and 2-bromodiethyl malonate. Buckyclutcher column (10 x 250 mm) – toluene 2 mL/min

The final reaction mixture contained mainly bis adducts (See Figure 4.25). According to the MALDI-TOF mass spectrum (See Figure 4.29) the last fraction contained tris adducts ($m/z=1715.12$) and tetra adducts ($m/z=1872.56$).

![Image](image2.png)

Figure 4.26 MALDI-TOF mass spectrum of diethylmalonate-[6,6]-Y₃N@I₆-C₈₀ tris adducts fraction
The most abundant bis adduct (peak with retention time of 27.5 min in Figure 4.25) was purified. The $^1$H NMR spectrum (See Figure 4.27) shows the signals corresponding to the methylene groups between 4.4 to 4.1 ppm, but their non equivalence produces a very complex pattern. The signals from the methyl groups are observed around 1.1 ppm (not shown). The chemical shift was deducted from the $^1$H COSY spectrum because they are overlapped with the contaminants present in CS$_2$. Very limited information can be obtained from NMR and crystallization was attempted without any success. The retention time was 14.7 min on a Buckyclutch (10 x 250mm) at 4 mL/min (See Figure 4.28). $m/z$:1557.8 (See Figure 4.29).

![Figure 4.27 500 MHz $^1$H NMR spectrum of diethylmalonate-[6,6]-Y$_3$N@I$_8$C$_{80}$ bis adduct (methylene region)](image-url)
Adding an addend to a [6,6] bond in the $I_h$-$C_{80}$ cage uses a pyrene type carbon from the 20 available (See Figure 1.2a), thus there are 19 remaining carbons that can react with the next addend. However, the pyrene type carbons are located at the junction of three [6,6] bonds so the addend can select any of the three available bonds in each intersection which can lead to 57 bis adducts (27 pairs of enantiomers and 3 highly symmetric structures) if symmetric malonates are used. The relatively low number of peaks in the
HPLC chromatogram might reflect some degree of regioselectivity for the second addition. However, at this point and without additional experimental results that conclusion remains speculative.
3. Electrochemical Properties

The electrochemical properties of the Bingel-Hirsch derivatives of \( \text{M}_3\text{N}@I_{h}-\text{C}_{80} \) (\( \text{M}=\text{Sc}, \text{Lu} \)) were measured in order to determine the effect of the functionalization. All the redox potentials are collected in Table 4.1. All the compounds have irreversible reductive electrochemical behavior as for the pristine TNT-EMFs\textsuperscript{28} (See Figure 4.30), but there are shifts in the reduction potentials. Compound 25 exhibits a 20 mV anodic shift. This is the result of periconjugation\textsuperscript{184,190} because the aromatic rings in the fluorene are held rigidly on the \( \text{Sc}_3\text{N}@I_{h}-\text{C}_{80} \) surface, so that the \( \pi \) orbitals of the fluorene can interact with the orbitals of the fullerene cage. The remaining \( \text{Sc}_3\text{N}@I_{h}-\text{C}_{80} \) derivatives (26, 28 and 29) have cathodic shifts of 80, 120 and 110 mV respectively, so they all have higher energy LUMOs. This is potentially advantageous for organic solar cell applications because higher energy LUMOs result in higher open circuit voltages.\textsuperscript{153}

Table 4.1 Redox potentials of Bingel-Hirsch-[6,6]-\( \text{M}_3\text{N}@I_{h}-\text{C}_{80} \) derivatives (\( \text{M}=\text{Sc}, \text{Lu} \)). All the values are reported in volts vs the Fc/Fc\textsuperscript{*} redox pair. Supporting electrolyte \( n\text{Bu}_4\text{NPF}_6 \) 0.050 M in \( o\)-DCB. Scan rate 100 mV/s, glassy carbon was the working electrode, Pt was the counter electrode and Ag wire was the reference.

<table>
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<th>Compound</th>
<th>( E^{+/+2} )</th>
<th>( E^{0/+} )</th>
<th>( E^{0/-} )</th>
<th>( E^{+/2-} )</th>
<th>( E^{2-/3-} )</th>
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<tr>
<td>( \text{Lu}<em>3\text{N}@I</em>{h}-\text{C}_{80} )\textsuperscript{152}</td>
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<td>+0.64</td>
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<td>-1.80</td>
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<td>-2.21</td>
</tr>
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</table>
Among the Sc₃N@I₆-C₈₀ mono adducts compound 29, which contains the amide functionality, has the highest reduction potential (-1.37 V vs -1.34 V); therefore, from the electronic point of view the amide adduct is the best option for preparing soluble Sc₃N@I₆-C₈₀ derivatives to be used directly as electron acceptors in the fabrication of organic solar cells. From the synthetic point of view compound 29 is also better because of its ease of preparation and purification. The Lu₃N@I₆-C₈₀ derivatives follow the same
trend. Compound 30 has a -1.49 V reduction potential, which is one of the highest reported values for fullerene mono adducts.

The formation of bis adducts seems advantageous in the case of Sc₃N@I₈-C₈₀ because the malonate bis adduct has a reduction potential 40 mV more negative than that of the mono derivative; however, for Lu₃N@I₈-C₈₀ the trend is not the same. Multiple addends disturb the electronic distribution on the fullerene surface and usually the poly adducts have higher reduction potentials than the mono adducts, but the charge transport diminishes.¹⁵⁴

Another important electrochemical property of the compounds prepared is that they are electrochemically stable both under reductive and oxidative conditions in contrast with other fulleropyrrolidines which are not stable under oxidative conditions.⁴³,¹⁵¹
4. Thermal stability studies of TNT-EMF derivatives

The materials used in the construction of solar cells are exposed to both high solar radiation and high temperatures. They have to be able to tolerate those harsh conditions for a reasonable amount of time in order to make that technology economically viable. For organic solar cells it has been estimated that modules with an efficiency of 7% should have a lifespan of at least seven years in order to be competitive with current technologies. Here we present thermogravimetric studies of two representative Sc$_3$N@I$_h$-C$_{80}$ derivatives: PCBM-[6,6]-Sc$_3$N@I$_h$-C$_{80}$ and N-tBu-[5,6]-Sc$_3$N@I$_h$-C$_{80}$ fulleropyrroidine and compare their thermal stability with that of phenyl-C$_{61}$-butyric acid methyl ester (PCBM), the most common fullerene derivative used in the fabrication of organic solar cells.

Phenyl-C$_{61}$-butyric acid methyl ester (PCBM) was obtained from Aldrich. PCBM-[6,6]-Sc$_3$N@I$_h$-C$_{80}$ was prepared according to literature methods. It has a 14.0 min retention time on a PBB column using toluene as eluent at 3 mL/min. $m/z$: 1299.56 (See Figure 4.32). The NMR data matches the reported values. Its $^1$H-$^{13}$C HSQC spectrum is shown in Figure 4.33.

Figure 4.31 HPLC trace of PCBM-[6,6]-Sc$_3$N@I$_h$-C$_{80}$. PBB column (4.6 x 250 mm) – toluene 3 mL/min
Figure 4.32 MALDI-TOF mass spectrum of PCBM-[6,6]-Sc₃N@I₈-C₈₀. Negative ionization mode (9-nitroanthracene as matrix)

Figure 4.33 ¹H-¹³C HSQC NMR spectrum of PCBM-[6,6]-Sc₃N@I₈-C₈₀
$N$-tBu-$[5,6]$-$\text{Sc}_3\text{N}^@I_5$-C$_{80}$ fulleropyrrolidine was prepared by reacting $N$-t-Butylglycine with Sc$_3$N$^@I_5$-C$_{80}$ and paraformaldehyde. The regiochemistry of the addition was verified by NMR. The HMQC spectrum (See Figure 4.34) of the product shows the correlation between the pyrrolidine proton signals at 3.02 and 3.98 ppm with a single carbon at 62.3 ppm which confirms unequivocally that the addition occurred on a [5,6] bond.

Figure 4.34 $^1\text{H}-^{13}\text{C}$-HMQC spectrum on $N$-tBu-$[5,6]$-$\text{Sc}_3\text{N}^@I_5$-C$_{80}$ fulleropyrrolidine
The mass of the addend in C_{60}-PCBM corresponds to 20.8% of the total mass of the sample. The TGA analysis (See Figure 4.35a) shows a mass loss smaller than 2% starting at 105°C and ending at 200°C that probably corresponds to residual solvent evaporation. Then the mass is stable until 375°C where the sample starts decomposing. There is an 11% mass loss which corresponds to only a partial mass of the addend. In the case of Sc_{3}N@I_{h}-C_{80}-PCBM (See Figure 4.35c) the mass of the addend corresponds to 14.6% of the total mass of the sample. Approximately 8% of the mass is lost between 140°C and 250°C. Then additional mass is lost slowly until 375°C where the decomposition of the fullerene starts. For N-tBu-[5,6]-Sc_{3}N@I_{h}-C_{80} fulleropyrrolidine (See Figure 4.35b) the mass of the addend corresponds to 8.2% of the total mass of the sample. There is a 4% mass loss that starts at 96°C and probably corresponds to residual solvent and a sharp
mass loss at 300°C corresponding exactly to the loss of the pyrrolidine; whereas the fullerene starts to decompose at 470°C.

Figure 4.36 Proposed mechanism for the thermal decomposition of TNT-EMF derivatives based on the TGA studies

TGA studies thus show that Sc₃N@I₆-C₈₀ derivatives are considerably less thermally resistant than PCBM. However, the typical solar cell operating temperatures are under 70°C so they could be suitable for the intended application.
5. Conclusions and Recommendations

New conditions for the preparation of Bingel-Hirsch derivatives of Sc$_3$N@I$_h$-C$_{80}$ and Lu$_3$N@I$_h$-C$_{80}$ were found. Among the three different substrates tested: fluorene, malonate ester and malonate bis amide, the amide is the best alternative because it can tolerate better the side hydrolysis reaction that occurs due to the presence of NaH to deprotonate the malonate derivative. Similar reactions should be attempted by changing either the base to lithium diisopropylamide (LDA) or to potassium tert-butoxide. The open cage fullerene derivatives obtained have higher reduction potentials than the pristine TNT-EMFs, therefore they are potentially useful acceptor materials in organic solar cells.

Poor regioselective control was found for the preparation of Y$_3$N@I$_h$-C$_{80}$ bis malonate derivatives. Thus a controlled bis or poly adduct formation has to be found in order to prepare derivatives with both higher reduction potentials and higher solubilities. For that purpose a tether controlled functionalization strategy may be useful. Thermo gravimetric analysis demonstrated that Sc$_3$N@I$_h$-C$_{80}$ derivatives are less thermally stable than PCBDM.
CHAPTER FIVE
PREPARATION OF PHOTOACTIVE FILMS BY ELECTROPOLYMERIZATION OF
TNT-EMFS DONOR ACCEPTOR SYSTEMS

1. Introduction

After 15 years of the discovery of bulk heterojunction solar cells, there has been considerable progress in the field. The basic operation principles are understood and efficiencies have risen from 2.9% to ~8%. Most of the research has been concentrated on finding new donor polymers and varying the donor:acceptor ratio. However, very few materials have been proposed as acceptors; therefore, both C₆₀-PCBM and C₇₀-PCBM continue to be the choice materials for the fabrication of organic solar cells.

One reason that makes PCBM derivatives difficult to replace is charge mobility because in organic semiconductors it is several orders of magnitude lower than for the inorganic counterparts. For example, hole mobility in silicon is 450 cm²V⁻¹s⁻¹ and electron mobility is 1400 cm²V⁻¹s⁻¹; this is in sharp contrast with the observed charge mobility in the materials used to fabricate organic solar cells. Hole mobility in P3HT is ~2.0*10⁻² cm²V⁻¹s⁻¹ and electron mobility in C₆₀-PCBM and C₇₀-PCBM is 0.21 cm²V⁻¹s⁻¹ and 0.1 cm²V⁻¹s⁻¹, respectively. That limits the maximum thickness to ~100 nm thus making the fabrication process more complex and the devices prone to fabrication defects. C₆₀-PCBM exhibits reasonably high electron mobility. C₆₀-PCBM bis adducts were proposed as alternative materials to take advantage of their higher energy LUMO, but the consequent decrease in electron mobility has prevented their use.
Another advantage of PCBM is solubility. $C_{60}$ and $C_{70}$ PCBMs are among the most soluble fullerene derivatives,\textsuperscript{193} which is a key requirement for the fabrication process, because bulk heterojunction organic solar cells are fabricated by spin coating or printing processes that requires ink materials with solubilities of $\sim 10 \text{ mg/mL}$.\textsuperscript{94} This parameter precludes many alternative materials including TNT-EMFs.

Electropolymerization is receiving increasing attention as an alternative method for the fabrication of organic solar cells,\textsuperscript{196} not only because it prevents the undesirable phase separation that affects the long time performance of organic solar cells,\textsuperscript{197} but also because the polymers grown by electro polymerization have conductances up to three orders of magnitude higher than the same polymer prepared by other methods.\textsuperscript{198} Additionally it allows the use of fullerene derivatives that are less soluble than PCBMs but with higher LUMO energy levels.\textsuperscript{196}

Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) PEDOT:PSS is used as the hole transporter layer in the best organic solar cells known today.\textsuperscript{95} The organic solar cell devices that use a layer of electro-polymerized PEDOT:PSS instead of the same material deposited by spin coating have higher efficiencies.\textsuperscript{199} Important donor materials such as porphyrins are also suitable for electro-polymerization and the resulting polymers are conductive.\textsuperscript{200}

Electropolymerization of triphenylamine derivatives has been explored for many years.\textsuperscript{201} The simplest monomer triphenylamine is not very effective and simply undergoes dimerization under oxidative conditions, but its more complex derivatives have been used successfully to prepare electrochemically deposited films that can even be
stacked to form multilayer arrangements. A preliminary observation during the electrochemical studies of the triphenylamine based donor acceptor systems described in Chapter 3 triggered the idea of electropolymerizing these derivatives and to test the resulting films for photovoltaic activity.

Electropolymerization of the triphenylamine moieties occurs only under oxidative conditions but the retro-cycloaddition reaction of fulleropyrrolidines occurs at similar potentials, therefore, the use of fulleropyrrolidines is not compatible. Therefore we decided to take advantage of the methodology we found to prepare Bingel-Hirsch derivatives of Sc$_3$N@$I_h$-C$_{80}$ and use that strategy to prepare two donor-acceptor systems that contain triphenylamine (TPA) and then electropolymerize them on conductive Indium Tin Oxide (ITO) electrodes under positive potentials. This should lead to double cable polymers that incorporate Sc$_3$N@$I_h$-C$_{80}$ within its structure.
2. Synthesis of the dyads

2.1. Synthesis of the precursors

Commercially available 4-(diphenylamino)benzaldehyde was reacted with aniline and sodium cyanoborohydride in order to prepare the secondary amine, 34. This compound was purified on a silica gel column eluting with toluene/ethyl acetate 9:1. It was obtained in 92% yield. $^1$H NMR (500 MHz, CDCl$_3$, TMS) $\delta$ 7.21 (m, 6H, ArH), 7.16 (m, 2H, ArH), 7.05 (m, 6H, ArH), 6.97 (t, 2H $^3$J$_{(H,H)}$ = 7 Hz, ArH), 6.70 (t, 1H $^3$J$_{(H,H)}$ = 7 Hz, ArH), 6.62 (d, 2H $^3$J$_{(H,H)}$ = 7 Hz, ArH), 4.22 (s, 2H, BzH), 3.93 (brs, 1H, NH). $^{13}$C NMR (125 MHz, CDCl$_3$, TMS) $\delta$ 148.15, 147.74, 146.96, 133.50, 129.21, 129.18, 128.51, 124.14, 124.09, 122.68, 117.48, 112.77, 47.87 (See Figure 5.2).
This amine was reacted with ethyl malonyl dichloride in the presence of triethylamine in CH$_2$Cl$_2$ at 0°C. The reaction mixture was washed with brine and extracted with CH$_2$Cl$_2$. The ethyl malonyl amide 35 was purified by column chromatography using silica gel as stationary phase and eluting with toluene/ethyl acetate 95:5. $^1$H NMR (500 MHz, CDCl$_3$, TMS) $\delta$ 7.35 (m, 2H, ArH), 7.24 (m, 4H, ArH), 7.06 (m, 8H, ArH), 6.98 (m, 5H, ArH), 4.86 (s, 2H, BzH), 4.12 (q, 2H, $^3$J$_{H,H} = 7$ Hz, O-CH$_2$), 3.21 (s, 2H, O-CH$_2$-CO), 1.22 (t, 3H, $^3$J$_{H,H} = 7$ Hz, -CH$_3$). $^{13}$C NMR (125 MHz, CDCl$_3$, TMS) $\delta$
This compound was mono brominated using CBr₄/DBU in CH₂Cl₂ to yield the ethyl 2-bromomalonyl amide derivative 36. This compound was purified on a silica gel column eluting with toluene.

1H NMR (500 MHz, CDCl₃, TMS) δ 7.37 (m, 2H, ArH), 7.26 (m, 4H, ArH), 7.09 (m, 8H, ArH), 7.01 (m, 5H, ArH), 4.95 (d, 1H, J(H,H) = 15 Hz, BzH), 4.89 (s, 1H, OCBRCH-CO), 4.83 (d, 1H, J(H,H) = 15 Hz, BzH), 4.15 (q, 2H, J(H,H) = 7 Hz, O-CH₂), 1.25 (t, 3H, J(H,H) = 7 Hz, -CH₃).

Using a similar approach secondary amine 34 was reacted with malonyl dichloride in the presence of triethylamine at 0°C. The malonyl bisamide 37 was purified on a silica gel column eluting with toluene/ethyl acetate 9:1 (49% yield). 1H NMR (500 MHz, CDCl₃, TMS) δ 7.21 (m, 14H, ArH), 7.04 (m, 12H, ArH), 6.97 (m, 8H, ArH), 6.79 (m, 4H, ArH), 4.77 (s, 4H, BzH), 3.00 (s, 2H, OC-CH₂-CO). 13C NMR (125 MHz, CDCl₃, TMS) δ 166.96, 147.64, 146.87, 141.90, 131.16, 129.70, 129.36, 129.09, 128.55, 127.94, 124.01, 123.75, 122.60, 52.44, 42.35.

This compound was mono brominated using CBr₄/DBU in CH₂Cl₂ to yield the 2-bromomalonyl bisamide 38. This compound was purified on a silica gel column eluting with toluene/ethyl acetate 9:1 (46% yield). 1H NMR (500 MHz, CDCl₃, TMS) δ 7.30 (m, 2H, ArH), 7.21 (m, 12H, ArH), 7.07-6.92 (m, 24H, ArH), 4.78 (d, 2H, J(H,H) = 15 Hz, BzH), 4.69 (s, 1H, OCBRCH-CO), 4.69 (d, 2H, J(H,H) = 15 Hz, BzH). 13C NMR (125 MHz, CDCl₃, TMS) δ 164.06, 147.66, 147.22, 140.58, 130.44, 130.18, 129.53, 129.25, 129.19, 128.45, 124.17, 123.65, 122.80, 54.06, 45.99 (See Figure 5.3).
Sc$_3$N@I$_h$-C$_{80}$ was prepared by arc discharge of graphite rods packed with graphite/Sc$_2$O$_3$/Cu in 7:2:1 ratio. The packed rods were annealed at 1000°C for 12 hours and arced using the reactive atmosphere method (200 Torr He / 10 Torr NH$_3$). The obtained soot was extracted with CS$_2$ and filtered using a short silica plug in order to remove the polyaromatic hydrocarbons. Sc$_3$N@I$_h$-C$_{80}$ was then purified using the procedure described in Chapter 2.
2.2. Synthesis of monoTPA-[6,6]-Sc$_3$N@I$_h$-C$_{80}$

![Synthesis of monoTPA-[6,6]-Sc$_3$N@I$_h$-C$_{80}$](image)

Figure 5.4 Synthesis of monoTPA-[6,6]-Sc$_3$N@I$_h$-C$_{80}$

3.6 mg of Sc$_3$N@I$_h$-C$_{80}$ (3.24 µmol, 1 eq) was poured together with 16.1 mg of compound 36 (29.4 µmol, 9 eq) and 20 mg of NaH (60% mineral oil suspension) in a Schlenk flask. 50 mL of anhydrous o-DCB/DMF solvent mixture 4:1 were added and the reaction mixture heated to 80°C overnight while stirring under argon. A preliminary purification step was made using a silica column using CS$_2$ in order to recover the unreacted Sc$_3$N@I$_h$-C$_{80}$ and the product was eluted with a mixture of toluene/ethyl acetate/triethylamine 90:9:1. After evaporating the fraction containing the desired product it was re-dissolved in toluene, filtered and separated using HPLC using a PBB column (4.6 x 250 mm) eluting with toluene 3 mL/min. Compound 39 has a retention time of 15.0 min (See Figure 5.5). $^1$H NMR (500 MHz, CS$_2$, Acetone-external): $\delta$ 7.42 (m, 3H, ArH), 7.19 (m, 5H, ArH), 7.09 (br, 2H, ArH), 6.96 (m, 7H, ArH), 6.84 (m, 2H, ArH), 4.94 (br, 2H, BzH). MALDI-TOF (Negative ionization mode – 9-nitroanthracene as matrix) $m/z$: 1500.2 (See Figure 5.6)
Figure 5.5 HPLC trace of compound 39. PBB column (4.6 x 250 mm) - toluene 3 mL/min

Figure 5.6 MALDI-TOF mass spectrum of compound 39. Negative ionization mode (9-nitroanthracene as matrix)
2.3. Synthesis of bisTPA-[6,6]-Sc$_3$N@I$_{h}$-C$_{80}$

![Image](image.png)

Figure 5.7 Synthesis of bisTPA-[6,6]-Sc$_3$N@I$_{h}$-C$_{80}$

9.0 mg of Sc$_3$N@I$_{h}$-C$_{80}$ (8.11 µmol, 1 eq) was poured together with 50.0 mg of compound 38 (59.0 µmol, 7.2 eq) and 28 mg of NaH (60% mineral oil suspension) in a Schlenk flask. 20 mL of anhydrous o-DCB/DMF solvent mixture 4:1 were added and the reaction mixture heated to 60°C overnight while stirring under argon. A preliminary purification step was made using a silica column using CS$_2$ in order to recover the unreacted Sc$_3$N@I$_{h}$-C$_{80}$ whereas the product was eluted with a mixture of toluene/ethyl acetate/triethylamine 90:9:1. Only 3.0 mg of Sc$_3$N@I$_{h}$-C$_{80}$ were consumed. After evaporating the fraction containing the desired product it was re-dissolved in toluene,
filtered and separated by HPLC using a PBB column (4.6 x 250 mm) eluting with toluene 2 mL/min. Compound 40 has a retention time of 24.8 min (See Figure 5.8).

Figure 5.8 HPLC trace of compound 40. PBB column (4.6 x 250 mm) - toluene 2 mL/min

Figure 5.9 MALDI-TOF mass spectrum of compound 40. Negative ionization mode. (9-nitroanthracene as matrix).
3. Electrochemical Properties

The electrochemical properties of the dyads were examined by cyclic voltammetry (CV) and Osteryoung Square Wave Voltammetry (OSWV). All the redox potentials are collected in Table 5.1. The reductive electrochemical behavior for both compound 39 and 40 is irreversible as for the pristine Sc$_3$N@I$_h$-C$_{80}$ (See Figure 5.10). As shown previously, this behavior is observed for all the Sc$_3$N@I$_h$-C$_{80}$-Bingel-Hirsch derivatives. There is a difference in the first reduction potential for compounds 39 and 40. Compound 39 is harder to reduce than pristine Sc$_3$N@I$_h$-C$_{80}$ by 90 mV as described previously for other Bingel-Hirsch adducts. However, compound 40 is easier to reduce than the pristine Sc$_3$N@I$_h$-C$_{80}$ by 10 mV. This difference is too small to suggest specific interactions between orbitals from the triphenylamine addend and those of the fullerene cage, but it may be possible because the triphenylamines are sterically bulky so some degree of steric hindrance may be present.

Table 5.1 Redox potentials of Bingel-Hirsch triphenylamine dyads. All the values are reported in volts vs the Fe/Fe$^+$ redox pair. Supporting electrolyte nBu$_4$NPF$_6$ 0.050 M in o-DCB. Scan rate 100 mV/s, glassy carbon working electrode, Pt counter, Ag wire as reference.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E^{+/-2}$</th>
<th>$E^{0/+}$</th>
<th>$E^{0/-}$</th>
<th>$E^{-2/-}$</th>
<th>$E^{2/-3/-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc$_3$N@I$<em>h$-C$</em>{80}$</td>
<td>+1.09</td>
<td>+0.59</td>
<td>-1.26</td>
<td>-1.62</td>
<td>-2.37</td>
</tr>
<tr>
<td>4-(diphenylamino)benzyl alcohol</td>
<td>-</td>
<td>+0.51</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Compound 39</td>
<td>+0.98</td>
<td>+0.54</td>
<td>-1.35</td>
<td>-1.70</td>
<td>-2.35</td>
</tr>
<tr>
<td>Compound 40</td>
<td>+0.99</td>
<td>+0.61</td>
<td>-1.25</td>
<td>-1.70</td>
<td>-2.29</td>
</tr>
</tbody>
</table>
Figure 5.10 Electrochemical studies of Bingel-Hirsch triphenylamine derivatives Left - Cyclic voltammograms of (a) Sc$_3$N@$I_x$-C$_{80}$ (b) Compound 39 (c) Compound 40 Right - Osteryoung Square Wave Voltammetry (OSWV) of (a) Sc$_3$N@$I_x$-C$_{80}$ (b) Compound 39 (c) Compound 40

The anodic scan exhibits a dominant oxidation process that overlaps with the first oxidation potential of Sc$_3$N@$I_x$-C$_{80}$. For that reason the peak looks larger than the others because the process involves not only the electron that is removed from the addend but also one electron from the fullerene cage. The second peak corresponds to the second oxidation process based on the fullerene cage. The anodic scans for both compound 39 and 40 resulted in a film on the working electrode. A detailed description of these observations is presented in the next section.
4. Oxidatively induced electropolymerization

Multiple scans at different potentials were made (See Figure 5.11) using the $N$-TPA-[5,6]-Sc$_3$N@I$_h$-C$_{80}$-fulleropyrrolidine described in chapter 3. It was observed than the polymerization occurs only at potentials above that for triphenylamine oxidation. Due to the presence of the triphenylamine in both compound 39 and compound 40, they can also be electrooxidatively polymerized.

Figure 5.11 Multiple scan cyclic voltammetry of $N$-TPA-[5,6]-Sc$_3$N@I$_h$-C$_{80}$-fulleropyrrolidine. (a) First oxidation process (b) second oxidation process (c) Third oxidation process (d) First reduction process (e) Second reduction process (f) Third reduction process. Working electrode glassy carbon, Pt as counter electrode and silver wire as reference. Tetrabutylammonium hexafluorophosphate 0.050 M in $o$-DCB was used as the supporting electrolyte/solvent system.
Growing films with $N$-TPA-[5,6]-Sc$_3$N@$I_h$-C$_{80}$-fulleropyrrolidine is not very interesting, because the properties of the resulting film will not be the same as those of the starting dyad since many of the dyad molecules will break during the electro-polymerization as consequence of the retro-cycloaddition reaction. However, the Bingel-Hirsch derivatives 39 and 40 are stable under oxidative conditions. For compound 39 the potential was cycled between -0.5 V and 1.0 V vs Fc/Fc$^+$ which produced a film on the glassy carbon working electrode (See Figure 5.12a). The same procedure was used for compound 40 but cycling the potential between -0.75 V and 1.0 V vs Fc/Fc$^+$ to have a similar result. Formation of the films also occurs when Pt is used as the working electrode. Interestingly, the film resulting from the bis TPA derivative grows considerably faster probably because the two TPA addends are involved in polymerization.

![Graph](image)

Figure 5.12 Electrooxidative-polymerization of triphenylamine Bingel-Hirsch derivatives of Sc$_3$N@$I_h$-C$_{80}$ (a) Compound 39 (b) Compound 40. Working electrode glassy carbon Pt as counter electrode and silver wire as reference. Tetrabutylammonium hexafluorophosphate 0.050 M in $o$-DCB was used as the supporting electrolyte/solvent system.
Compound 39 was used to deposit a film on a patterned transparent ITO electrode (See Figure 5.13). The deposition process was simple; the ITO was used as the working electrode and the potential cycled 80 times between the same potentials used with the glassy carbon. At the end of the deposition process the current stopped increasing. This phenomenon was initially attributed to the passivation of the polymer film. However, after analyzing the film it was noticed that it remains conductive and that the passivation actually occurred on the Pt counter electrode. Once the film was formed it was washed with CH₂Cl₂ to remove the residual electrolyte and dried under nitrogen. This film can be stored under air without loosing its properties.

Figure 5.13 Trimetallic nitride endohedral metallofullerene photoactive film preparation (a) Background with bare ITO electrode and electrolyte (b) oxidative electro-polymerization process (c) Patterned ITO electrode before the deposition (d) photoactive film
5. Characterization of the films

The electropolymerized film of compound 39 was characterized by atomic force microscopy (AFM) (See Figure 5.14). The profile shows that the film has an average thickness of 120 nm. This is an excellent result because the film remains conductive hence it can be made thicker if necessary, which will result in enhanced light absorption and charge carrier generation that should translate into higher efficiencies. The differential UV-VIS spectrum of the film (after subtracting the spectrum of the ITO electrode) shows absorption only in the UV range (See Figure 5.15).

Figure 5.14 AFM images of the electrooxidatively polymerized film for compound 39. (a), (c) and (d) AFM images (b) thickness measurement rms 120nm.
Figure 5.15 UV-VIS spectrum of the electro deposited film of compound 39 on a transparent ITO electrode

This was expected because neither the triphenylamine nor the Sc₃N@I₈-C₈₀ has strong absorptions in the visible range of the spectrum.

Figure 5.16 Open circuit voltage of a cell built using a film of compound 39

A solar cell device was built using the electro-polymerized film of compound 39. The film was immersed in a 0.050 M solution of tetra(n-butyl)ammonium
hexafluorophosphate in o-DCB and a platinum electrode also immersed in the solution completed the circuit. No electron transport intermediate redox system was used. After degassing the solution with argon, the cell was poured in the dark and irradiated with a 420 nm lamp for 1 minute periods while following the open circuit voltage (See Figure 5.16)

![Diagram of molecular structure](image)

Figure 5.17 Possible structure of the film formed by compound 39.

A clear photovoltaic effect was observed even though there is no electron blocking layer on top of the ITO electrode. This result is very encouraging and can be a basis to build organic solar cell devices that exploit the superior physical and electronic properties of TNT-EMFs compared to empty cage fullerenes.
6. Conclusions and Recommendations

The preparation of air stable films on transparent ITO electrodes incorporating trimetallic nitride endohedral metallofullerenes was achieved. The photovoltaic properties of one of the resulting films were evaluated and it was found that the film does generate electricity when it is irradiated with light. The thickness of the film has an rms value of 120 nm, which is within the commonly used range for the preparation of organic solar cells. The UV-VIS spectrum shows that the film has relatively poor light absorption in the visible range, thus its efficiency may be limited by this property.

It is recommended that a layer of PEDOT:PSS or a triphenylamine derivative be electrodeposited on the ITO as an electron blocking layer before starting the electropolymerization of the fullerene derivative in order to prevent short circuits in the cell. The same principle should be applied to the counter electrode and a layer of LiF as hole blocking layer is recommended.

It would also be interesting to incorporate a porphyrin or a phthalocyanine in the structure in order to enhance the light absorption in the visible range.
CHAPTER SIX
ELECTROCHEMICAL PROPERTIES OF METALLIC AND METALLIC OXIDE
ENDOHEDRAL METALLO FULLERENES

1. Introduction

The discovery of trimetallic nitride endohedral metallofullerenes (TNT-EMFs)\(^1\) not only allowed the preparation of bulk amounts of fullerenes containing encapsulated metals, but also showed the possibility of encapsulating atom clusters inside fullerene cages. Today the charge transfer stabilization principle behind the formation of endohedral fullerene species is understood\(^{62,74,130,203,204}\) and new metal clusters encapsulated in fullerene cages have been reported. It started in 2001 with the metal carbide endohedral metallofullerene family,\(^{205}\) and quickly this family was expanded\(^{206-211}\) and their stability was also explained based on the same principle of charge transfer from the endohedral cluster towards the fullerene cage.\(^{212}\) More recently endohedral fullerenes encapsulating oxygenated clusters\(^{213-215}\) and metal sulfides were found.\(^{216,217}\)

The properties of the trimetallic nitride endohedral fullerenes are strongly influenced by the encapsulated cluster;\(^7\) therefore finding new fullerenes encapsulating different atom clusters is of great interest for the development of new materials with similar or even better properties that the ones already observed for other endohedral metallofullerenes.

In this chapter we describe the optimization of the parameters for the preparation of metal sulfide endohedral fullerenes (MSEFs) using the method recently reported by our
group that uses SO\textsubscript{2} as the source of sulfur.\textsuperscript{217} The electrochemical properties of two Sc\textsubscript{2}S@C\textsubscript{82} isomers\textsuperscript{217} were studied and compared to those of Sc\textsubscript{4}O\textsubscript{2}@I\textsubscript{h}-C\textsubscript{80}\textsuperscript{213-215} which was isolated from a fullerene mixture sample sent to us by Professor Steven Stevenson and M\textsubscript{3}N@I\textsubscript{h}-C\textsubscript{80} (M=Sc, Lu) prepared in our lab in order to study the influence of the cluster in the electrochemical properties of the endohedral metallofullerenes. Some of the results obtained here were published in the following article:

2. Preparation of metallic sulfide endohedral fullerenes (MSEFs)

$\text{Sc}_2\text{S}^@\text{C}_{2n}$ ($n = 41, 42$) were prepared in a Kräschmer–Huffman reactor by evaporating $\frac{1}{4}$” diameter graphite rods packed with mixtures of $\text{Sc}_2\text{O}_3$ and graphite in 5:95, 15:85 and 25:75 ratios using a 200 Torr atmosphere of He/SO$_2$ with 190:10, 180:20 and 170:30 ratios. The rods were annealed at 1000°C for 12 hours in a nitrogen atmosphere before arcing. The voltage gap during the arcing was kept between 30 to 32 VDC and 3 rods were evaporated under each set of conditions. The soot was extracted with CS$_2$ and the extract filtered using a 7 cm x 10 cm diameter Büchner funnel half filled with silica gel. The solution was evaporated and the resulting gray solid was washed with acetone and ethyl acetate in order to remove the poly-aromatic hydrocarbons and the elemental sulfur that was found in the extracts. This sulfur is formed presumably in the plasma during the arcing process by reduction of SO$_2$. The black solid residue which contains the fullerenes was re-dissolved in toluene filtered and separated by HPLC using first a Buckyprep-M (10 x 250 mm) followed by a Buckyprep (10x 250 mm) column eluting with toluene (4 mL/min).

The mass of packing material used for each rod and the current circulating during the arcing depend on the amount of $\text{Sc}_2\text{O}_3$ used because it is denser than graphite so the rods with higher graphite content are lighter than the ones containing higher amounts of $\text{Sc}_2\text{O}_3$. On the other hand, $\text{Sc}_2\text{O}_3$ helps to decrease the resistance of the rods. That may be a consequence of the partial reduction of $\text{Sc}_2\text{O}_3$ during the annealing of the rods. Therefore metallic scandium is probably responsible for enhancing the conductance of the rods hence the current during the arcing process (See Table 6.1).
Table 6.1 Arcing conditions for the preparation of metallic sulfide endohedral metallofullerenes used during the optimization.

<table>
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<th>Pressure SO$_2$ (Torr)</th>
<th>5% w/w Sc$_2$O$_3$</th>
<th>15% w/w Sc$_2$O$_3$</th>
<th>25% w/w Sc$_2$O$_3$</th>
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<td>10</td>
<td>2.28 g of packed material. Arcing current 75-80A</td>
<td>2.45 g of packed material. Arcing current 85-90A</td>
<td>3.12 g of packed material. Arcing current 90-100A</td>
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The partial pressure of SO$_2$ was selected considering that the optimal conditions for the preparation of trimetallic nitride endohedral metallofullerenes, widely studied in our lab, uses 20 Torr of NH$_3$. It is well known that the presence of oxygen has a negative effect on the yield of fullerenes prepared using the arcing method. It was even suggested that SO$_2$ could not be used for the preparation of sulfur containing endohedral metallofullerenes. However, preliminary experiments demonstrated the successful formation of MSEFs when 20 Torr SO$_2$ was introduced in the gas mixture. One of our goals was then to determine whether higher or lower SO$_2$ content would increase the yield of MSEFs.

The rods packing content can affect the fullerene yield because it affects the final composition of the rod after annealing, the mass of the rod, the electrical parameters, the plasma temperature and the formation of deposits in the cathode during the arcing. The 3:1 graphite/Sc$_2$O$_3$ ratio has been successfully used in our lab for the preparation of Sc$_3$N@I$_{h}$-C$_{80}$; however, those conditions may not necessarily correspond to the optimal conditions for the preparation of other endohedral metallofullerene families. The actual
amount of Sc$_2$O$_3$ used for packing each rod is also important due to the cost of the materials; it is desirable to use as little as possible.

![Figure 6.1 Influence of SO$_2$ in the formation of MSEFs followed by HPLC. (a) 5% Sc$_2$O$_3$ (b) 15% Sc$_2$O$_3$ (c) 25% Sc$_2$O$_3$. The black boxes denote the peaks corresponding to empty cage fullerenes and the numbers denote the fractions collected which contain the MSEFs.](image)

It was observed that high SO$_2$ concentration decreases the total fullerene yield especially that of empty cages then it has a similar effect to that of ammonia in the preparation of trimetallic nitride endohedral metallofullerenes when the reactive atmosphere method is used\textsuperscript{11} but in this case SO$_2$ also has a negative effect in the
formation of MSEFs. However, the effect of Sc$_2$O$_3$ in the packing mixture is more noticeable. For example, when the rods are packed with 25% Sc$_2$O$_3$, the SO$_2$ does not have a significant effect in the total fullerene yield and a high content of Sc$_2$O$_3$ in the rod seems to protect the fullerenes from the negative effect of the high SO$_2$ concentration (See Figure 6.1c and Figure 6.2c).

![Graphs showing influence of Sc$_2$O$_3$ in MSEF formation](image)

**Figure 6.2** Influence of the Sc$_2$O$_3$ in the formation of MSEFs followed by HPLC. (a) 10 Torr SO$_2$ (b) 20 Torr SO$_2$ (c) 30 Torr SO$_2$. The black boxes denote the peaks corresponding to empty cage fullerenes whereas the numbers denote the fractions collected which contain the MSEFs.
Low contents of Sc$_2$O$_3$ favor not only the total fullerene yield, but also the formation of MSEFs (See Figure 6.1a, Figure 6.1b, Figure 6.2a and Figure 6.2b). The fullerene production with low contents of Sc$_2$O$_3$ is only affected if a relatively high content of SO$_2$ is used in the gas mixture introduced in the reactor (See Figure 6.2c). Thus based on the previous observations a low content of Sc$_2$O$_3$ and a low concentration of SO$_2$ are the best conditions for the preparation of MSEFs. However, before selecting the ideal Sc$_2$O$_3$ content and SO$_2$ partial pressure other experimental parameters were considered.

As it was discussed before, the rods packed with low contents of Sc$_2$O$_3$ are less conductive so the total current circulating is lower because the voltage gap was constant in all the experiments. This has a negative effect in the arcing process because the electric arc is not stable. On the other hand if the current is too high erosion rather than evaporation of the electrodes occurs and the total fullerene yield is also affected.

Previous experience with the preparation of TNT-EMFs in our lab has allowed us to determine a current of 85A as the ideal value for a clean evaporation of a ¼” graphite rod. Therefore 10% w/w Sc$_2$O$_3$ and 10 Torr of SO$_2$ were established as the ideal conditions for the preparation of MSEFs. Using these optimized conditions, 450 mg of fullerene mixture was produced after evaporating twelve ¼” diameter rods. This result is very significant because it demonstrates that MSEFs can be prepared with higher yields than TNT-EMFs.

Sc$_4$O$_2@I_p$-$C_{80}$ was separated in two steps using a PBB column (4.6 x 250 mm) eluting with toluene/o-DCB 95:5 at 2.0 mL/min (See Figure Figure 6.3).
Figure 6.3 HPLC purification of Sc₄O₂@I₆-C₈₀. PBB column (4.6 x 250 mm) mobile phase toluene/o-DCB 95:5 (a) Starting fullerene mixture as received from Professor Steven Stevenson (b) Chromatogram after first stage (c) Peak after second stage. The boxes represent the collected fractions in each step.

Figure 6.4 MALDI-TOF mass spectrum of Sc₄O₂@I₆-C₈₀. Negative ionization mode – 9-nitroanthracene as matrix.
3. Electrochemical Properties

The electrochemical properties of two \( \text{Sc}_2\text{S@C}_{82} \) isomers (\( C_s \) and \( C_{3v} \)) and \( \text{Sc}_4\text{O}_2@I_{h-}\text{C}_{80} \) were studied by cyclic voltammetry CV and Osteryoung Square Wave Voltammetry (OSWV) experiments and compared to those of \( \text{Sc}_3\text{N}@I_{h-}\text{C}_{80} \). All the redox potentials are listed in Table 6.2. All the experiments were carried out using solutions of \( n\text{Bu}_4\text{NPF}_6 \) 0.050 M in \( \sigma\)-DCB at a scan rate of 100 mV/s using a glassy carbon electrode as working electrode, a Pt wire as counter and a silver wire as pseudo-reference.

![Figure 6.5](image_url)

Figure 6.5 Electrochemical studies of scandium metallofullerenes containing different clusters. Left - Cyclic voltammograms of (a) \( \text{Sc}_2\text{S@C}_{82} \) (b) \( \text{Sc}_2\text{S@C}_{3v-}\text{C}_{82} \) (c) \( \text{Sc}_4\text{O}_2@I_{h-}\text{C}_{80} \) (d) \( \text{Sc}_3\text{N}@I_{h-}\text{C}_{80} \). Right - Osteryoung Square Wave Voltammetry (OSWV) of (e) \( \text{Sc}_2\text{S@C}_{82} \) (f) \( \text{Sc}_2\text{S@C}_{3v-}\text{C}_{82} \) (g) \( \text{Sc}_4\text{O}_2@I_{h-}\text{C}_{80} \) (h) \( \text{Sc}_3\text{N}@I_{h-}\text{C}_{80} \).
The electrochemical studies show the strong influence of the encapsulated cluster in the electrochemistry of endohedral metallofullerenes. When comparing \( \text{Sc}_4O_2@I_h-C_{80} \) and \( \text{Sc}_3N@I_h-C_{80} \), although the fullerene cage is the same, \( \text{Sc}_4O_2@I_h-C_{80} \) exhibits reversible reductive electrochemical behavior, but not the other. Theoretical calculations indicate that the LUMO in \( \text{Sc}_4O_2@I_h-C_{80} \) is located on the cluster similarly to what has been observed for \( \text{Sc}_3N@I_h-C_{80} \).\(^{215}\)

Table 6.2 Redox potentials of scandium endohedral metallofullerenes. All the values are reported in volts vs the Fc/Fc\(^+\) redox pair. Supporting electrolyte \( n\text{Bu}_4\text{NPF}_6\) 0.050 M in \( o\)-DCB. Scan rate 100 mV/s, glassy carbon working electrode, Pt counter, Ag wire as reference.

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<th>Compound</th>
<th>( E^{+2/+3} )</th>
<th>( E^{+/+2} )</th>
<th>( E^{0/+} )</th>
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<th>( E^{+/-} )</th>
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<td>( \text{Sc}<em>2S@C_5-C</em>{82} )</td>
<td>+0.98</td>
<td>+0.65</td>
<td>+0.43</td>
<td>-1.03</td>
<td>-1.18</td>
<td>-1.79</td>
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<tr>
<td>( \text{Sc}<em>2S@C</em>{3v}-C_{82} )</td>
<td>-</td>
<td>+0.96</td>
<td>+0.52</td>
<td>-1.04</td>
<td>-1.19</td>
<td>-1.63</td>
<td>-2.49</td>
</tr>
<tr>
<td>( \text{Sc}<em>4O_2@I_h-C</em>{80} )</td>
<td>-</td>
<td>+0.79</td>
<td>+0.00</td>
<td>-1.10</td>
<td>-1.73</td>
<td>-2.35</td>
<td>-</td>
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<tr>
<td>( \text{Sc}<em>4C_2@I_h-C</em>{80} )</td>
<td>-</td>
<td>+1.10</td>
<td>+0.40</td>
<td>-1.16</td>
<td>-1.65</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( \text{Sc}<em>3N@I_h-C</em>{80} )</td>
<td>-</td>
<td>+1.09</td>
<td>+0.59</td>
<td>-1.26</td>
<td>-1.62</td>
<td>-2.37</td>
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In the oxidative scan \( \text{Sc}_4O_2@I_h-C_{80} \) display two reversible oxidation processes and again there is a clear difference with the behavior of \( \text{Sc}_3N@I_h-C_{80} \). The first oxidation process is occurring at 0.00 V vs Fc/Fc\(^+\). The reason behind this may be related with the formal charge in the metal atoms in the \( \text{Sc}_4O_2^{6+} \) cluster, because in order for this cluster to have a 6+ charge, two Sc atoms must have a 3+ charge and 2 Sc atoms a 2+ charge,\(^{214}\) then the two oxidation processes would be related to the oxidation of two Sc atoms from
Sc$^{2+}$ to Sc$^{3+}$ and the HOMO and HOMO+1 would be located on the metal cluster with a small contribution from the fullerene cage. The electrochemical behavior of Sc$_4$C$_2@I_h$-C$_{80}$ also supports this conclusion because it has been calculated that the Sc atoms in the Sc$_4$C$_2$ cluster have a 3+ charge and the first oxidation for this fullerene occurs at +0.40 V.

The Sc$_2$S@C$_{82}$ isomers exhibit different electrochemical behavior. In the reductive scan the $C_5$ isomer has three reversible reduction processes and the first two are separated by just 150 mV. For the $C_{3v}$ isomer, the first two reductions are occurring at similar potentials, but the first one is irreversible. In the anodic scan the two isomers also have dissimilar behavior, so since these fullerenes have the same metal cluster the results suggest that the differences observed are a consequence of the different carbon cages.

The reversible electrochemical behavior of the most abundant Sc$_2$S@C$_5$-C$_{82}$ isomer is an advantage for potential organic solar cell applications, but the first reduction potential is 230 mV lower than that for Sc$_3$N@I$_{h}$-C$_{80}$ and 390 mV lower than that for Lu$_3$N@I$_{h}$-C$_{80}$ which would have a bad impact in the open circuit voltage. On the other hand the presence of sulfur in the cluster may have a good effect enhancing the conductance properties of the fullerene material.
4. Conclusions and Recommendations

Metal sulfide endohedral metallofullerenes can be prepared in higher yields than Sc$_3$N@I$_h$-C$_{80}$ (the most abundant trimetallic nitride endohedral metallofullerene) by introducing SO$_2$ in the arcing atmosphere. However, high concentrations of SO$_2$ have a negative effect in the yield of this new endohedral metallofullerene family. The amount of Sc$_2$O$_3$ packed in the graphite rods has stronger influence in the total yield of fullerene species and low concentrations $\leq 10\%$ should be used for packing the rods in order to ensure a high fullerene yield.

Scandium endohedral metallofullerenes have different electrochemical behavior even if they share the same fullerene cage, then encapsulating new clusters is of great interest for the development of new fullerene materials with a wide variety of electrochemical properties. The chemical functionalization of Sc$_4$O$_2$@I$_h$-C$_{80}$ and Sc$_2$S@C$_{82}$ species should be studied in order to obtain materials more suitable for the intended applications and in order to study the effect of chemical functionalization in the electrochemical properties which probably will be different than those of the pristine fullerenes based on what has been observed in the case of trimetallic nitride endohedral metallofullerenes.$^{28}$
SUMMARY AND CONCLUSIONS

Trimetallic nitride endohedral metallofullerenes were successfully functionalized with diverse donor molecules obtaining donor – acceptor systems with potential application in the fabrication of organic solar cells. The evaluation of the photophysical properties of some of the compounds, conducted by Professor Dirk Guldi in Germany, revealed that trimetallic nitride endohedral metallofullerenes are better than C_{60} at stabilizing the charge separated states generated upon light irradiation of the donor – acceptor systems. However, the 1,3-dipolar cycloaddition reaction used in most of the cases for connecting the donor and acceptor moieties is not a good strategy for the preparation of these systems because the fulleropyrrolidine rings are not stable under oxidative conditions and the dyads decompose easily.

The influence of the bridge connecting the donor moiety and the fullerene used as acceptor was studied in two fulleropyrrolidines with a σ bridge and with three molecules with a molecular wire used as bridge to favor the long distance charge separation. In the first case when the donor was connected to the nitrogen atom on the pyrrolidine ring the charge separated state can live longer than the one where the donor is connected to the 2-position of the pyrrolidine ring. In the second case the longer molecular wire (40 Å from center to center) yielded the longer lived charge separated state as expected. The preparation of donor – acceptor systems using the multiple redox steps strategy has to be done in order to further improve the lifetime of the charge separated states. A combination of a redox gradient with a molecular wire could be even more advantageous in order to separate the charges as efficiently as possible at long distances.
The optimal conditions for the preparation of Bingel-Hirsch derivatives of $\text{M}_3\text{N}@[I_h]_8\text{C}_{80}$ (M=Lu and Sc) were found. The amides of malonic acid are the most suitable derivatives due to the harsh conditions used. The obtained derivatives exhibit irreversible electrochemical behavior just as the pristine TNT-EMFs do.

The electro-oxidative polymerization of donor acceptor systems containing triphenylamine and $\text{Sc}_3\text{N}@[I_h]_8\text{C}_{80}$ was made on ITO electrodes. The polymeric film obtained is photo-active and has the typical thickness found in organic solar cells. This methodology is suggested as a strategy for incorporating low solubility donor – acceptor systems not suitable for printing processes and as a good way to control the microstructure and the charge mobility in the cell (the most important parameters affecting the efficiency of the current organic solar cells).

Finally, optimization of the production of metal sulfide endohedral metallofullerenes was made. Now we can produce these fullerenes in yields that exceed those of trimetallic nitride endohedral metallofullerenes; therefore, this would be the solution to encapsulate metals such as Gd or Lu which have interesting applications but they are typically encapsulated in low yields in trimetallic nitride endohedral metallofullerenes.
References


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