Metal Nitride Cluster Fullerene $M_3N@C_{80}$ ($M = Y$, Sc) Based Dyads: Synthesis, and Electrochemical, Theoretical and Photophysical Studies


Abstract: The first pyrrolidine and cyclopropane derivatives of the trimetallic nitride templated (TNT) endohedral metallofullerenes $I_2$-Sc$_3N@C_{80}$ and $I_2$-Y$_3N@C_{80}$ connected to an electron-donor unit (i.e., tetrathiafulvalene, phthalocyanine or ferrocene) were successfully prepared by 1,3-dipolar cycloaddition reactions of azomethine ylides and Bingel-Hirsch-type reactions. Electrochemical studies confirmed the formation of the [6,6] regioisomers for the Y$_3N@C_{80}$-based dyads and the [5,6] regioisomers in the case of Sc$_3N@C_{80}$-based dyads. Similar to other TNT endohedral metallofullerene systems previously synthesized, irreversible reductive behavior was observed for the [6,6]-Y$_3N@C_{80}$-based dyads, whereas the [5,6]-Sc$_3N@C_{80}$-based dyads exhibited reversible reductive electrochemistry. Density functional calculations were also carried out on these dyads confirming the importance of these structures as electron transfer model systems. Furthermore, photophysical investigations on a ferrocenyl–Sc$_3N@C_{80}$- fulleropyrrolidine dyad demonstrated the existence of a photoinduced electron-transfer process that yields a radical ion pair with a lifetime three times longer than that obtained for the analogous C$_{60}$ dyad.

Keywords: donor–acceptor dyads · electrochemistry · fullerenes · metal–nitride clusters · photophysics

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Introduction

Carbon nanostructures such as fullerene\cite{1,2} and carbon nanotubes (CNTs)\cite{10} represent a fascinating class of materials which are attracting considerable attention due to their potential technological applications,\cite{1} More recently, a wide variety of new carbon nanostructures, including endohedral fullerenes, have emerged as new and exciting carbon-containing materials whose chemical and physical properties are currently being explored.\cite{4} Among the endohedral fullerenes,\cite{5,6} the trivalent nitride templated (TNT) endohedral metallofullerenes—carbon cages that encapsulate trivalent nitride clusters—have been the focus of great interest since their first synthesis in 1999 by the process developed by Dorn and co-workers.\cite{6} This method has allowed the preparation of TNT endohedral metallofullerenes in high yields. The stabilization of a large variety of endohedral carbon cages, including different isomeric structures or compounds that violate the isolated pentagon rule has been realized, simply by the judicious choice of the trapped metal atoms.\cite{7} In addition, due to their interesting physical properties TNT endohedral metallofullerenes have been investigated for potential applications in the fields of biomedicine and nanomaterials sciences.\cite{8}

Derivatization of these fullerene species is essential to construct novel organo-metallofullerene materials for a variety of future applications. To date, however, reports on the exohedral derivatization of TNT endohedral metallofullerenes are scarce and only a few types of reactions (Diels–Alder,\cite{9,10} 1,3-dipolar cycloaddition of azomethine ylides,\cite{10} Bingel–Hirsch-type,\cite{11} disilirane addition,\cite{12} radical trifluoromethylation\cite{13} and malonate free radicals\cite{14,15}) have been reported. The experimental and theoretical studies carried out on these TNT endohedral fullerenes suggest that the chemical reactivity and regioselectivity observed are a consequence of several parameters such as the nature of the encapsulated metal cluster, the carbon cage size, and the symmetry of the endohedral fullerene itself.

A fundamental aspect of TNT endohedral metallofullerenes, which yet awaits exploration, is their possible application in electron donor–acceptor (D–A) systems.\cite{15} Although C_{60} fullerene and higher homologue structures have been extensively incorporated into D–A systems due to their low reorganization energies in charge-transfer processes, as well as their significant electron-mobility features, acting as excellent electron acceptors,\cite{16} only one example of the TNT endohedral fullerenes has ever been explored in this context.\cite{17} In addition, TNT endohedral metallofullerenes possess larger absorptive coefficients than C_{60} in the visible region of the electromagnetic spectrum and a low HOMO–LUMO energy gap, while preserving a remarkable electron accepting ability, similar to that of C_{60}.\cite{5}

In the present work, a series of M_3N@C_{60} (M = Y, Sc) based D–A dyads have been synthesized via 1,3-dipolar cycloaddition reactions of azomethine ylides or Bingel–Hirsch-type reactions. Three different types of donor moieties have been considered in our investigations: i) ferrocene (Fc) derivatives,\cite{18} ii) extended tetrahexalvalene (exTTF) derivatives,\cite{19} which exhibit strong stabilization upon oxidation as they gain aromaticity and planarity in the process, thus stabilizing the photolytically generated radical ion pairs in D–A systems and; iii) phthalocyanine (Pcs) derivatives, which are aromatic macrocycles possessing extinction coefficients as high as 200000 \( \text{cm}^{-1} \cdot \text{mol}^{-1} \) in the 700 nm range.\cite{20} The chemical reactivity investigations of the \( I_2\cdot \text{Se}_3\text{N@C}_{60} \) and \( I_2\cdot \text{Y}_3\text{N@C}_{60} \) cages towards the construction of D–A systems were complemented with electrochemical, theoretical, and photophysical studies.

Results and Discussion

Synthesis: The first synthetic strategy pursued for the preparation of M_3N@C_{60}-based dyads (M = Y, Sc) was based on the 1,3-dipolar cycloaddition reaction of azomethine ylides, to give rise to a pyrrolidine adduct on the endohedral fullerene moiety (Scheme 1).\cite{21} Cycloaddition reactions of azomethine ylides on endohedral metallofullerenes have been reported, showing different selectivity depending on the metal cluster.\cite{19} Two types of C–C double bonds are available on the M_3N@C_{60} cage (M = Y, Sc) for the reaction with the in situ generated azomethine ylide: the C–C double bonds between two hexagonal rings ([6,6]-junctions) and those between pentagonal and hexagonal rings ([5,6]-junctions). When the fullerene inner metal cluster was Sc_3N, the only product detected was the adduct at a [5,6]-junction. On the other hand, the 1,3-dipolar cycloaddition reaction occurred at a [6,6]-junction for the Y_3N@C_{60}. The Y_3N@C_{60} [6,6]-monoadducts proved to be the kinetic products, and they underwent rearrangement to the thermodynamically more stable Y_3N@C_{60} [5,6]-monoadducts upon heating.\cite{22} Recently, both the [6,6] and [5,6]pyrrolidine monoadducts of Sc_3N@C_{60} were isolated when an N-trityl azomethine ylide was employed instead of the N-methyl or N-ethyl analogues.\cite{23,24} These experimental results, as well as recent computational studies by Poblet and Echegoyen,\cite{23} seem to indicate that after thermalization of the kinetically favored product, a pirouette-kind of mechanism gives rise to the [5,6]-monoadduct that is thermodynamically preferred. The rate of this rearrangement depends on the internal cluster and on the pyrrolidine addend.

The reactivity of the TNT species proved to be very different to that of empty cage fullerenes and thus the synthetic protocol required adjustments to prepare the desired TNT dyads. An initial attempt to prepare a Pc-substituted pyrrolidine-containing Sc_3N@C_{60} dyad following the procedures optimized for other Sc_3N@C_{60} pyrrolidines\cite{19a} was not very effective and only traces of the Pc dyad were obtained after heating for 50 min at 120°C (Figure S1). Similar attempts to prepare the Pc-substituted Y_3N@C_{60} dyad 3 provided some insight into the actual reaction path. In this case the reaction was allowed to go for 5 h and a side product was isolated which did not contain the Pc unit. In fact, fur-
Unfortunately, Pc-substituted pyrrolidine-containing Y3N@C80 dyad 3 decomposes under ambient conditions giving rise to the parent endohedral metallofullerene (Y3N@C80) and no further characterization was possible. It has been demonstrated that fulleropyrrolidine adducts undergo retro-1,3-dipolar cycloadditions under thermal and electrochemically oxidative conditions. The retro-cycloaddition reaction seems to happen even faster in the case of Y3N@C80 derivatives containing with electron donor units, probably due to their marked difference in electronic character. However, when considering ferrocene carboxaldehyde as precursor of the donor unit in the 1,3-dipolar cycloaddition reaction of azomethine ylides to form M3N@C80-based dyads, the stability of the obtained compounds (4 and 5) was found to be quite different from that of compound 3. After reacting Y3N@C80 with N-methylglycine and ferrocene carboxaldehyde 2, the formation of multiple adducts was observed. Nonetheless, the major fraction was isolated by using preparative silica gel TLC and found to correspond to the N-methyl-2-ferrocenyl-[6,6]-I-Y3N@C80-fulleropyrrolidine (5). This dyad exhibits a 9.3 min retention time on a Buckycutcher column eluting with toluene (4 mL min−1) (see Figure S5). The regioselective 1,3-dipolar cycloaddition reaction at a [6,6] bond was inferred from the irreversible electrochemistry of the isolated adduct (see Electrochemical Section).

The 1H NMR spectrum of compound 5 shows individual resonances for the protons of the cyclopentadienyl (Cp) ring directly attached to the pyrrolidine ring in the region between δ 4.6 and 4.25 ppm (Figure 1b). The geminal protons on the pyrrolidine ring appear as two doublets separated by ≈1.2 ppm due to the asymmetry introduced by the ferrocenyl group. One of the doublets (J(H,H) = 9.6 Hz) overlaps with the singlet originating from the unsubstituted Cp ring at 4.19 ppm, while the other one is observed at 3.0 ppm. The remaining proton in the pyrrolidine ring appears as a singlet at δ 3.63 ppm while the N-methyl group is observed as a singlet at 3.14 ppm. The presence of only one set of signals for the pyrrolidine protons clearly indicates that we only have one pair of enantiomers out of the possible two, or that at least one pair of them was present in a higher proportion and the less abundant pair was not detected by 1H NMR (Figure 1b). No other significant signals were observed, implying that the carbon of the pyrrolidine ring next to the ferrocene unit shows a preference for either the pyrene-like or coronene-like carbon. There are many examples illustrating the regioselectivity of the 1,3-dipolar cycloaddition reactions over asymmetric olefin substrates (before copper catalysts were developed) in which the attack of the dipole is strongly influenced by steric and electronic factors. Surprisingly, when compound 5 was heated at 150°C, instead of the expected isomerization of the [6,6] adduct to the [5,6] adduct—as previously observed in similar systems—a retro-cycloaddition reaction to give back IY3N@C80 was observed. The sensitivity of adduct 5 to light and temperature was also evident in the MALDI-TOF mass spectrum where only the peak corresponding to Y3N@C80+ was ob-

Scheme 1. Synthesis of pyrrolidine-based TNT endohedral metallofullerenes substituted with different donor-bearing aldehydes.
served even though 9-nitroanthracene was used as matrix and the analysis was performed in negative ionization mode (Figure S6).[9a]

When aldehyde 2 was reacted with \( \text{I}_3\text{Sc,N@C}_{80} \) in the presence of N-methylglycine, adduct 4 was formed. This dyad showed a retention time of 11.53 min on a Bucky-clutcher column (toluene 4 mL/min/cell) and reversible electrolysis which suggests that it was the \([5,6]\) regioisomer (see Electrochemical Section).[17] The \(^1\)H NMR spectrum of this adduct shows individual resonances for the protons in the Cp ring attached directly to the pyrrolidine in the region from \( \delta 4.60 \) to \( 4.25 \) ppm (Figure 1a). The pyrrolidine geminal protons are separated by \( \approx 1.2 \) ppm and appear as doublets at \( 4.18 \) and \( 3.01 \) ppm (\( J = 9.5 \) Hz). The proton on the methine carbon appears at \( 3.61 \) ppm, while the N-methyl protons appear as a singlet at \( 3.14 \) ppm. The coupling between the protons in the Cp ring was evident in the COSY spectrum. By HMQC the carbons with protons attached to them could be assigned. The MALDI-TOF mass spectrum of compound 4 was obtained by using 9-nitroanthracene as matrix and running in negative ionization mode showed the molecular ion peak but also the peak corresponding to the fragment \( \text{Sc,N@C}_{80}^{+} \). Dyad 4, in contrast with the other pyrrolidine-based \( \text{Y,N@C}_{80} \) (M = Sc, Y) dyads (3 and 5) was found to be relatively stable at room temperature for over two months.

In an attempt to prepare other types of TNT endohedral fullerene-based dyads, we decided to test the Bingel–Hirsch reaction on \( \text{Y,N@C}_{80} \) since the corresponding \([6,6]\)-open di(ethoxycarbonyl)methano adducts withstand thermal as well as reductive/oxidative electrolytic conditions, while \( \text{I}_3\text{Sc,N@C}_{80} \) did not react under the same experimental conditions.[11] Taking advantage of the proven stability of the \( \text{Y,N@C}_{80} \) malonate fullerenoids, two dyad systems were prepared by following the Bingel–Hirsch protocol (Scheme 2).

Compound 6[31] was reacted with \( \text{Y,N@C}_{80} \) in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) resulting in the formation of the desired exTTF-containing adduct 7 (see Experimental Section for details). Interestingly, the \(^1\)H NMR spectrum of compound 7 showed the benzylic protons appearing as two sets of doublets centered at \( 5.60 \) ppm (\( J \approx 12 \) Hz), both of them distorted due to the roof effect (Figure 2b). The observed splitting pattern is due to: i) the exTTF moiety adopting a “butterfly” conformation in which the 1,3-dithiolene groups are bent out of the plane of the anthracene core, creating two different magnetic envi-

![Figure 1. 1H NMR spectra of a) 4 in CS$_2$/D$_2$-DCB and b) 5 in CS$_2$/D$_6$acetone. The insets show the pair of enantiomers formed by addition of the addend at a [5,6]-junction in a) and the two possible isomers by addition of the addend at a [6,6]-junction in b): the pyrrolidine carbon atom holding the ferrocenyl moiety could be attached to a pyrene-like carbon or to a corannulene-like carbon. * The signal in the box of Figure 1b denotes impurities from the solvent.](image)

![Scheme 2. Synthesis of the Y,N@C$_{80}$ Bingel derivatives 7, 8 and 11.](image)
environments for the benzylic protons[31] and, ii) the slow rota-
tion of the exTTF group and the absence of a symmetry
plane bisecting the [6,6] bonds of the
Ih
-Y3N@C80 cage
which gives rise to two different magnetic environments.

Dyad
7
oxidized spontaneously and was transformed into
compound
8
in CHCl 3 solution within a few hours, first
losing one of the two 1,3-dithiolene groups leading to a very
unstable intermediate with a retention time of 18.3 min on
HPLC (Figure S7). The loss of the first dithiolene group is
followed by the loss of the other 1,3-dithiolene group, ulti-

mately producing the stable adduct
8
containing an anthra-
quinone moiety. This conclusion is supported by the
MALDI-TOF mass spectrum of each individual HPLC frac-
tion collected (Figure S8).

The 1H NMR spectrum of compound
8
shows the benzylic
protons as a set of doublets at 5.70 ppm due to hindered ro-
tation of the anthraquinone moiety, confirming the presence
of a “butterfly” conformation for the exTTF in the parent
compound
7
(Figure 2c). The absence of the vinyl protons
signal, added to the fact that all the aromatic signals were
downfield compared to those for the parent compound sup-
ported our conclusion. The electrochemical characterization
further confirmed the structure proposed for adduct
8
(see Electrochemical Section). The decomposition of dyad
7
seems to be the result of a photo-degradation process simi-
lar to the one reported for other exTTF analogues,[32] since
protecting the sample from light slows down the conversion
of
7
into
8.

For preparation of Pc-based dyad
11,
compound
10
was
prepared from tri-tert-butylhydroxymethyl-phthalocyanina-
tozinc(II)[33] 9
(see Experimental Section for details). Compound
10
was reacted with
Y3N@C80
in the presence of
DBU yielding dyad
11. Unfortunately, compound
11
was
not stable and decomposed in
CHCl 3 solution under our ex-
perimental conditions during the
purification process. The forma-
tion and degradation of
11
was followed by HPLC
as shown in Figure 3. We were
able to characterize the two
major degradation products, giving insight into the process.
One of these was the
Y3N@C80-diethylmalonic acid adduct; its MALDI-TOF mass
spectrum (Figure 4) resembles the one obtained after treat-
ing the
Y3N@C80-diethylmalonate adduct with metallic sodium,[11a]
where the molecular ion peak is not observed because of frag-
mentation, which gives a peak corresponding to the mass of
Y3N@C81 ++, while its HPLC re-

Figure 2. 1H NMR spectra for a) 6 in CDCl 3 , b) 7 in CS 2 /CDCl 3 4:1 and c) 8 in CS 2 /CDCl 3 4:1. The methyl sig-
sals observed at high field are overlapped with grease and solvent impurities and are omitted for clarity. Circle in a) denotes residual toluene after purification and a solvent impurity in b).

Figure 3. HPLC chromatograms (Buckyclutcher toluene 4 mL min −1) of:
a) Y3N@C80, b) 11 and, c) Y3N@C80 monoethyl malonate adduct obtained
by decomposition of dyad
11.
rification methods need to be explored in order to construct robust dyads based on these endohedral carbon cages.

**Electrochemistry**: The electrochemical properties of compounds 4, 5, 7 and 8 were investigated by cyclic voltammetry at room temperature in o-DCB solutions. Their redox potentials are collected in Tables 1 and 2 (see below), along with those of 2, exTTF-CHO, and 2-hydroxymethylanthraquinone (AQ-CH₂OH), C₆₀, I₇-Y₃N@C₈₀ and several [5,6] and [6,6]pyrrolidine or metallofullerene adducts of I₇-Y₃N@C₈₀ or Y₃N@C₈₀ as references.

The I₇-Y₃N@C₈₀ and Y₃N@C₈₀ cages exhibit irreversible redox processes at a scan rate of 100 mVs⁻¹, although the reductive electrochemistry of I₇-Y₃N@C₈₀ becomes reversible at higher scan rates.²⁴,²⁵ It has also been previously shown that the general electrochemical behavior of M₃N@C₈₀ derivatives can be employed to differentiate between the two regioisomers formed at [5,6]- and [6,6]-bonds.²² Reversible electrochemical cathodic behaviors have been observed for [5,6]-monoadducts, whereas the corresponding [6,6]-monoadducts show irreversible behaviors. In line with these considerations, Figure 5 shows representative CVs for the exTTF-based dyad 7, and the anthraquinone–Y₃N@C₈₀ Bingel derivative 8. Dyad 7 exhibits the typical electrochemical behavior of [6,6]-methanofullerene derivatives of Y₃N@C₈₀,²³ that is, an irreversible reductive behavior as shown in Figure 5 (trace a). On the oxidation side, the quasi-reversible processes of the respective parent metallofullerene and exTTF²⁶ are observed at +0.90 and +0.23 V, respectively.

The cyclic voltammogram of anthraquinone–Y₃N@C₈₀ Bingel adduct 8 shows two reduction and one oxidation waves, corresponding to the reductions of the anthraquinone moiety, and the oxidation of the Y₃N@C₈₀ cage, respectively (Figure 5, trace b). The first reduction step at −1.34 V was found to be electrochemically reversible. The second reduction step at −1.72 V and the oxidation step at +0.67 V were found to be electrochemically quasi-reversible by cyclic voltammetry. The shoulders observed at about −1.23 and −1.98 V probably correspond to the reduction of the C₈₀ cage, since the reductive processes of both fragments (Table 1, entries Y₃N@C₈₀ and AQ-CH₂OH) occur almost at the same potential. The absence of the oxidation process corresponding to the exTTF addend, and the presence of the two reduction waves of the anthraquinone addend, clearly demonstrated the conversion of exTTF into the anthraquinone adduct of Y₃N@C₈₀.

The electrochemical reductions of the pyrrolidinofullerene ferrocenyl monoadducts of I₇-SeC₃N@C₈₀ and I₇-Y₃N@C₈₀ 5 show different reversibility at a scan rate of 100 mVs⁻¹ (Figure 6). This indicates the formation of the different regioisomers: ferrocenyl [6,6]- and [5,6]fulleropyrrolidine of I₇-Y₃N@C₈₀ and I₇-SeC₃N@C₈₀, respectively.²⁵ Three one-electron reversible reductions at −1.14, −1.53, and −2.25 V were observed for the N-methyl-2-ferrocenyl-[5,6]-I₇-SeC₃N@C₈₀...
Table 2. Electrochemical oxidation potentials [V] vs Fc/Fc⁺ (o-DCB, 0.05 M nBu4NPF6) of compounds 2, 4, 5, 7, 8, exTTF-CHO. Values in brackets indicate peak to peak separation in mV. All values indicate half wave potentials unless indicated. First oxidation assigned to Sc3N@C80, brackets indicate peak to peak separation in mV. All values indicate half oxidation of the adduct.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Addend-based E°⁺</th>
<th>C80-cage-based E°⁺</th>
<th>E°/2⁺⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>2, Sc3N@C80³⁺</td>
<td>–</td>
<td>+0.59</td>
<td>–</td>
</tr>
<tr>
<td>4, Y3N@C80³⁺</td>
<td>–</td>
<td>+0.64</td>
<td>–</td>
</tr>
<tr>
<td>[6,6]-pyrrolidine–Sc3N@C80</td>
<td>–</td>
<td>+0.62</td>
<td>–</td>
</tr>
<tr>
<td>C237n³⁺</td>
<td>–</td>
<td>+0.65</td>
<td>–</td>
</tr>
<tr>
<td>[6,6]-pyrrolidine–Y3N@C80</td>
<td>+0.00</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>7</td>
<td>+0.23</td>
<td>–</td>
<td>+0.90</td>
</tr>
<tr>
<td>8</td>
<td>–</td>
<td>+0.67(131)</td>
<td>–</td>
</tr>
<tr>
<td>4</td>
<td>+0.15</td>
<td>+0.61(82)</td>
<td>+1.09(170)</td>
</tr>
<tr>
<td>5</td>
<td>+0.07</td>
<td>+0.57(141)</td>
<td>+0.66(96)</td>
</tr>
<tr>
<td>2</td>
<td>+0.20(117)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>exTTF-CHO</td>
<td>+0.06</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

[a] From ref. [22].  [b] Oxidation peak potential, irreversible process.  [c] Not well defined.

Figure 6. Cyclic voltammograms recorded on a GC electrode (1 mm) in o-DCB containing 0.05 M nBu4NPF6 as supporting electrolyte and a scan rate of 100 mV s⁻¹ for: a) 5; b) 7, Sc3N@C80 isomer and, c) 4.

Figure 7. Optimized structures of the down isomer of derivative 7 (left) and the anthraquinone derivative 8 (right).

We have analyzed in detail the electronic structure for the down isomer of derivative 7. As expected by the strong electron donating character of the TTF moiety, the HOMO is localized in this unit whereas the LUMO is localized in the fullerene part of the dyad (Figure S9). In particular, the LUMO is mainly localized in the carbon atoms of the cage being very similar to the LUMO observed for other Y3N@C60 fulleropyrrolidine compounds and the parent Y3N@C60 cage (Figure S9). The energy of the LUMO in these fullerene systems is actually not very different (within 0.3 eV at our computational level, Table 3). As a consequence, the first reduction peaks in the corresponding CVs should appear at similar reduction potentials as shown experimentally (see Table 1). The triplet state in which one electron is transferred from the donor unit (exTTF) to the acceptor C80-fulleropyrrolidine (4) (Figure 6, trace c). Additionally, in the positive potential range three oxidations were observed at +0.15, +0.61, and +1.09 V. The first process at +0.15 V corresponds to the oxidation of the ferrocenyl addend and the processes at +0.61 and +1.09 V are the oxidations of the fullerene cage.

Similar electrochemical behavior was observed for the oxidation of the ferrocenyl addend (+0.07 V) in 5, since the oxidation of this donor was found to be irreversible by cyclic voltammetry with the re-oxidation shifted about 380 mV in the direction of the negative potential. Two pairs of oxidations were observed for 5 at +0.57 and +0.66 V, one of them can be attributed to the cage-based oxidation of the adduct 5 while the other is possibly a result of electrochemical retrocycloaddition reaction which has been observed in case of pyrrolidino derivatives of Sc3N@C80.²⁷₈
moiety (metallofullerene), that is, the state with the charge separation, is computed to lay at much higher energies (around 30 kcal mol\(^{-1}\)). A plot of the spin density for this triplet state is shown in Figure S10.

For derivative 8, in contrast to what happens for \(Y_3\text{N@C}_{50}\)-exTTF dyad 7, the HOMO is localized in the fullerene part because the anthraquinone moiety is not as strong as an electron donor like the TTF derivatives. The LUMO is also localized on the fullerene moiety and it is very similar to the LUMO found in dyad 7. Indeed, these two LUMOs show very similar energies (Table 3). The LUMO +1, however, is localized on the anthraquinone (Figure S11, top) and is only 0.15 eV less stable than the LUMO. Therefore, it is not straightforward to predict from the energy of the molecular orbitals the localization site of the electron, that is, whether it will be in the anthraquinone moiety or in the carbon cage, once the neutral system has been reduced (see reduction processes for 8 on Figure 5, trace b).

It is important to note that the HOMO–LUMO gaps do not provide the experimental electrochemical gaps obtained from CV, although a correlation exists. The experimental electrochemical gap for dyad 7 is 1.51 V and the computed HOMO–LUMO gap is only 0.33 eV. It is possible, however, to estimate the electrochemical gap from computations (see Experimental Section). The theoretical electrochemical gap for dyad 7 was computed to be 1.47 V, very close to the experimental one.

Finally, we have carried out theoretical studies in order to analyze the relative stability of the different regioisomers and conformers of dyads 4 and 5, as well as their electronic structures and the nature of their frontier orbitals (Figure S12). The contributions to the total spin density of the different groups that constitute the dyads are collated in Table 4. In particular, 38% of the spin density is distributed between the \(M_3\text{N}\) unit and the fullerene cage for \(M = Sc\) (Figure S13a) whereas it is fully delocalized in the fullerene framework for \(M = Y\) (Figure S13b). The contributions to the total spin density of the different groups that constitute the dyads are collated in Table 4. In particular, 38% of the spin density is located on the \(Sc\)-N unit and 60% in the carbon framework for the \(Sc\)-based dyad. For \(M = Y\), however, the extra electron is mostly located on the carbon cage (91%) with a very small contribution to the total spin density from the \(Y_3\text{N}\) unit (5%).

To further assess the validity of our methodology, the difference in the first reduction potentials of dyads 4 and 5 was computed (see Experimental Section). The predicted value, 260 mV in the gas phase and 225 mV in o-DCB solution, agrees well with the experimental value of 200 mV.

### Table 3. Energy values [eV] for the HOMO and LUMO of structures 4, 5, 7, 8 and reference systems.

<table>
<thead>
<tr>
<th>Compound</th>
<th>HOMO</th>
<th>LUMO</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_{50})</td>
<td>–6.25</td>
<td>–4.55</td>
</tr>
<tr>
<td>(Y_3\text{ScN@C}_{50})</td>
<td>–5.78</td>
<td>–4.59</td>
</tr>
<tr>
<td>(Y_3\text{ScN@C}_{50}{[5,6]})-pyrrolidine</td>
<td>–5.50</td>
<td>–4.41</td>
</tr>
<tr>
<td>4</td>
<td>–4.60</td>
<td>–4.27</td>
</tr>
<tr>
<td>(Y_3\text{YN@C}_{50})</td>
<td>–5.92</td>
<td>–4.36</td>
</tr>
<tr>
<td>(Y_3\text{YN@C}_{50}{[6,6]})-methano adduct</td>
<td>–5.77</td>
<td>–4.26</td>
</tr>
<tr>
<td>7</td>
<td>–4.41</td>
<td>–4.08</td>
</tr>
<tr>
<td>8</td>
<td>–5.71</td>
<td>–4.21</td>
</tr>
<tr>
<td>5</td>
<td>–4.69</td>
<td>–4.14</td>
</tr>
</tbody>
</table>

Figure 8. Optimized structures, schematic diagrams and relative energies for the two possible isomers of \(N\)-methyl-2-ferrocenyl-[6,6]-\(Y_3\text{N@C}_{50}\)-fulleropyrrolidine 5 (corannulene on the left and pyrene on the right).
er, we have not been able to compute the electronic structure of the oxidized dyads for 4 and 5 due to the limitations of the mono-reference wavefunctions used in DFT. Multireference methods such as CASSCF or CASPT2 would be required, but the large dimensions of the dyads make them unattainable.

Table 4. Sum of the atomic spin densities (Mulliken partition) for each of the different groups in the reduced dyads 4 and 5.

<table>
<thead>
<tr>
<th></th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>M3N</td>
<td>0.383</td>
<td>0.050</td>
</tr>
<tr>
<td>pyrrolidine</td>
<td>0.016</td>
<td>0.037</td>
</tr>
<tr>
<td>fullerene</td>
<td>0.600</td>
<td>0.911</td>
</tr>
<tr>
<td>ferrocene</td>
<td>0.001</td>
<td>0.002</td>
</tr>
</tbody>
</table>

To sum up, the computed HOMO and LUMO energies (Table 3) are able to explain the general trends of the CVs. Dyads 4, 5 and 7, with very good electron-donor groups, show higher HOMO energies (around 1 eV) than the pristine M3N@C60 EMFs or the functionalized fulleropyrrolidines without these groups. On the other hand, the LUMO energies of the dyads and those of pristine or functionalized EMFs are similar, in good agreement with their analogous topologies. Therefore, the electrochemical gaps for EMF-based dyads are much smaller than for their EMF counterparts. For some dyads, we have checked that the inclusion of some degree of exact exchange in the density functional yields much larger HOMO–LUMO gaps but provides the same qualitative information.

Photophysical studies: The properties of the excited states of 4 were analyzed by means of different photophysical techniques and compared to those of reference compound I<sub>7</sub>-Sc-N@C60. In the absorption spectra we see a broad onset in the near-infrared (NIR) region. As a complement to the absorption experiments we turned to fluorescence experiments. I<sub>7</sub>-Sc-N@C60 exhibits weak fluorescence features—as a kind of mirror image to the ground state absorption—with an apparent maximum at 833 nm. Correspondingly, we derive a singlet excited state energy of 1.5 eV. Attachment of the electron donating ferrocene group leads to a complete quenching of the I<sub>7</sub>-Sc-N@C60 centered fluorescence. Implicit is a deactivation that involves either electron transfer, energy transfer or heavy ion quenching. It is also interesting that upon photoexciting I<sub>7</sub>-Sc-N@C60—lacking the electron donating ferrocene—a significant quantity of singlet oxygen (0.55) was found in NIR emission experiments, which was, however, completely abolished in the dyad.

The lack of detectable fluorescence in time-resolved experiments—seen even for I<sub>7</sub>-Sc-N@C60—led us to probe both compounds in transient absorption measurements. For I<sub>7</sub>-Sc-N@C60, the following features emerge: maxima at 508/1040 nm and a minimum at 650 nm. These are assigned to the singlet excited state of Sc-N@C60. From the corresponding multi-wavelength analyses we derived a surprisingly short singlet excited state lifetime (i.e., 48 ps), typical values found for C60 and C<sub>60</sub> derivatives are on the order of 1.5 ns. Nevertheless, the product of this the fast decay is the corresponding triplet excited state.

We finally turned to time-resolved transient absorption spectroscopy with 4. Initially we do observe the I<sub>7</sub>-Sc-N@C60 centered singlet excited state features, which decay quite rapidly. In fact, a singlet excited state lifetime of only 5 ps—a value that is well in line with the close donor–acceptor separation—has been determined for the Fc-substituted I<sub>7</sub>-Sc-N@C60. Moreover, the fast decay is associated with marked changes in the differential absorption spectrum. As Figure 10 illustrates, the singlet excited state features (i.e., maxima at 550 and 870 nm) transform over the course of 5 ps into a new set of maxima, which evolve in the visible region (i.e., 530 and 626 nm) as well as in the NIR region (i.e., 830 and 1120 nm).

Radiolytically and spectroelectrochemically generated spectra of the one-electron reduced I<sub>7</sub>-Sc-N@C60 radical anion (Figure 11) helped in the spectroscopic identification of the photoproduct. Of particular importance is the close resemblance with the photolytically generated spectrum, especially in the NIR part. In the visible portion, features of the one-electron oxidized ferrocenium evolve around 680 nm. Taking this into consideration, we conclude the successful formation of the radical ion pair state. The energy of approximately 1.29 eV has been estimated based on the electrochemically determined redox potentials. In other words, its formation starting from the I<sub>7</sub>-Sc-N@C60 singlet
excited state is thermodynamically feasible. The time-absorption profiles in Figure 10b also corroborate that the radical ion pair state is metastable decaying with a lifetime of 128 ps in carbon disulfide and 84 ps in o-DCB.

Testing a comparable C_{60} D–A conjugate, that is a ferroocene-based C_{60} dyad, under exactly the same experimental conditions—concentration, solvents and excitation energy—helped to appreciate the impact that using the Ih-Sc_{3}N@C_{80} exerts on the stabilization of the radical ion pair state. [18] In the tested solvents (i.e., CS_{2}, THF, and benzonitrile) we see the initially formed C_{60} singlet excited state with a transient maximum at 950 nm rapidly transforming (4.8 ps in THF) into the radical ion pair state. Maxima at 490 and 1010 nm are unequivocal attributes of the one-electron reduced C_{60} moiety, while the general signature of the one-electron oxidized ferrocene is seen around 680 nm. An illustration is provided in Figure S14. The corresponding lifetimes are 46 ps in CS_{2}, 49 ps in THF and 27 ps in benzonitrile.

**Conclusion**

We have explored the chemical reactivity of Ih-Sc_{3}N@C_{80} and Ih-Y_{3}N@C_{80} to prepare electron transfer model systems with suitable electron-donors, such as tetrathiafulvalene, phthalocyanine, and ferrocene, using 1,3-dipolar cycloaddi-
and potential performance in solar-energy conversion systems.

Experimental Section

General: Ferrocene carboxaldehyde (2) was purchased from Aldrich Chemical Co. Tri-tert-butylhydroxymethylphthalocyaninato-zinc(II), [33] tri-tert-butyl-(benzaldehyde-4-ethyl)phthalocyaninatozinc(II) (I) [4], [28]-dichlorobenzene (DCB) with 0.2 mol fraction (5) \( m\text{-methylene}-9,10-bis(1,3-dithiol-2-ylidine)-9,10-dihydro-anthra-

cene,[31] and 9,10-bis(1,3-dithiol-2-ylidine)-9,10-dihydro-2-antracenonyl-

dihydro-methyl-2-bromoethyle malonate[32] were prepared according to pub-
lished procedures. \( I_2 \) was obtained from the isomer mixture of \( I_3 \) and \( D_m \).

Sc\(_2\)N@C\(_8\)O were provided by Luna Innovations (Nanoworks division).

All reactions were run under an argon atmosphere and fol-
lowed by TLC on silica plates. Anhydrous solvents were purchased from
Aldrich and used as received. NMR spectra were obtained using Bruker
Avance 500 or Bruker Avance 300 spectrometers using TMS or residual
solvent signals as internal reference. MALDI-TOF mass spectrum was
obtained in a Voyager-DE STR mass spectrometer. Preparative TLC
was performed using Sorbent silica Gprep w/U254 500 \textmu \text{m preparative TLC
plates. HPLC was performed using a Varian Prostar equipped with a
buckyprop-M column and in a Varian Prostar 210 equipped with a buck-
yclutter column.

Theoretical calculations: The calculations were carried out by using DFT
methodology with the ADF 2006 program.[41] The exchange-correlation
functions of Becke and Perdew were used.[42] Relativistic corrections
were included by means of the ZORA formalism. Triplet-\( \zeta \) polarization
basis sets were employed to describe the valence electrons of the C, N,
O, S, Sc, Fe, and Y atoms. Frozen cores consisting of: i) the 1s shell for
C, N, O; ii) the 1s to 2p shells for S, Sc and Fe; and iii) the 1s to 3d shells
for Y were described by means of single Slater functions. The calcula-
tions were based on the oxidation of SCN\(^-\) to (SCN)\(_2\) which in aqueous
\( \text{N}_2\text{O}_5\)-saturated solution takes place with \( G^f\) = 6 (G denotes the number of
concentrations per 100 eV, or the approximate \% concentration per 1.0 eV absorbed energy).

The radical concentration generated per pulse was varied be-
tween (1−3) \(-10^{-6}\). Tri-tert-butyl(monoethyl ester malonate)phthalocyaninatozinc(II) (9): A flask was charged under argon with \( \text{CH}_2\text{Cl}_2 \) (6 mL), \( \text{EtN}_3 \) (31.3 mg,
0.31 mmol) and tri-tert-butylhydroxymethylphthalocyaninato-
zinc(II)[33] (60.0 mg, 0.06 mmol). The solution was then sonicated for 5 min
and solution of 3-chloro-3-ethyl-5-methyl-4-pyridine (6 mg, 0.01 mmol)
in \( \text{CH}_2\text{Cl}_2 \) (1 mL) added slowly to the solution while stirring. The solution
was let to stir at room temperature for 5 h. and then reduced in volume.

The crude product was purified by flash column chromatography (SiO\(_2\),
toluene/\( \text{EtOAc} \) 3:1) to afford the \( \text{Pc} \) as a dark-green solid (62 mg,
90\%). \( R_f = 0.71 \) (toluene/\( \text{EtOAc} \) 3:1); m.p. > 300°C. \( \text{HMR} \) (300 MHz,
\( \text{D}_2\text{DMSO} \), 25°C; residual solvent: \( \delta = 9.4−9.0 \) (br, 8H, Ar\(_8\)), 8.41−8.25
(br, 3H, Ar\(_8\)), 8.19−7.95 (br, 1H, Ar\(_8\)), 5.71 (s, 2H; \( \text{CH} \)), 4.28−4.12 (m,
2H), 3.82 (s, 2H), 1.78 (s, 27H; \( \text{Bu} \)), 1.36–1.31 ppm (m, 3H); UV/Vis
(\( \text{CHCl}_3 \)): \( \lambda_{\text{max}} = \{\log e\} = 286 \) (4.39), 340 (4.59), 609 (4.68), 643 (shoulder
(3.98), 677 nm (4.86); MALDI-TOF MS (for \( \text{C}_{148}\text{H}_{286}\text{N}_{10}\text{O}_{8}\text{Zn}; \text{FW} = 8904.96\); dithiolane; \( ml/z \% \)): 888.3−895.3 (isotopic pattern (100) \[ M^+ \], 1776.6−1786.6 (isotopic pattern (5) \[ 2M^+ \].

2-Bromo-ethyl-[tri-tert-butylhydroxymethylphthalocyaninatozinc(II)]: A flask was charged under argon with \( \text{Pc} \) (20 mg, 0.02 mmol), \( \text{CBr}_4 \) (74.5 mg, 0.22 mmol) and \( \text{CH}_2\text{Cl}_2 \) (5 mL) added. The solution was then cooled down to 0°C for 10 min to 10 min while stirring. After this time a solution of DBU (3.0 mm, 0.03 mmol) in \( \text{CH}_2\text{Cl}_2 \) (1 mL) was added slowly to the solution while stirring for 1 h. at 0°C. After this time the solu-
tion was let to reach room temperature, diluted with \( \text{CH}_2\text{Cl}_2 \) (50 mL) and washed with \( \text{HCl} \) (15 mL, 0.01 N) and brine (2×15 mL). The organic layer was then dried over \( \text{MgSO}_4 \), filtered and reduced in volume to obtain a green powder that was purified by preparative TLC (Merck,
silica gel-60, 0.5 mm; toluene/\( \text{EtOAc} \) 3:1) to obtain the \( \text{Pc} \) as a green powder
(8%. \( R_f = 0.82 \) (toluene/\( \text{EtOAc} \) 3:1); m.p. > 300°C. \( \text{HMR} \) (300 MHz,
\( \text{D}_2\text{DMSO} \), 25°C; residual solvent: \( \delta = 9.4−9.0 \) (br, 8H, Ar\(_8\)), 8.41−8.25
(br, 3H, Ar\(_8\)), 8.19−7.95 (br, 1H, Ar\(_8\)), 5.73 (s, 2H; \( \text{CH} \)), 4.95 (s, 1H; \( \text{CHBr} \)), 4.28−4.12 (m,
2H), 1.78 (s, 27H; \( \text{Bu} \)), 1.36−1.31 ppm (m, 3H); UV/Vis
(\( \text{CHCl}_3 \)): \( \lambda_{\text{max}} = \{\log e\} = 286 \) (286), 340 (4.59), 609 (4.68), 643 (shoulder
(3.98), 677 nm (4.86); MALDI-TOF MS (for \( \text{C}_{148}\text{H}_{286}\text{N}_{10}\text{O}_{8}\text{Zn}; \text{FW} = 8904.96\); dithiolane; \( ml/z \% \)): 888.3−895.3 (isotopic pattern (100) \[ M^+ \], 1776.6−1786.6 (isotopic pattern (5) \[ 2M^+ \].

N-Methyl-2-[tri-tert-butyl-(phenyl-4-ethyl)phthalocyaninato-zinc(II)]-
\( \text{Y}_N\text{C}\(_9\text{N}_2\); fulleropyrroolidine (3): An excess of N-methylglycine (1.91 mg,

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0.21 mmol, 4.4 equiv) and tri-tert-butyl-(benzaldehyde-4-ethynyl)phthalocyaninatozinc (II) (2)\(^{20}\). (35.40 mg, 0.0440 mmol, 8.3 fold) were placed in a flask containing dried molecular sieves (1 g, 4 Å) under argon. Then DMF (5 mL) was added and the mixture was stirred for 10 min. Then, a solution of I\(_2\)-Y\(_N\)-C\(_{80}\) (0.51 mmol, 1 equiv) in \(\sigma\)-DCB (10 mL) was added and the mixture stirred for 30 min at RT. Then, the reaction was heated to 120°C under argon. The progress of the reaction was followed by TLC and took about 2 h and 25 min to complete. The reaction mixture was then filtered and toluene (75 mL) was added to the filtrate. The resulting solution was extracted with water and brine; the organic layer was dried over MgSO\(_4\), and the solvent was removed under vacuum. The resulting residue was purified by column chromatography (SiO\(_2\), C\(_{18}\), followed by C\(_{18}\)/CHCl\(_3\) 1:1, and then CHCl\(_3\)/EtOAc 20:1) and monooadduct 5 was obtained (0.5 mg, 5%) after HPLC purification. HPLC retention time (Buckyprep-M, 1% pyridine/toluene 4 mL/min): \(t_r\) = 12.45 min; MALDI-TOF (positive mode): \(m/z\) = 2153.96 (base peak), 1298 M\(^+\) –(CH\(_3\)CH=CO) no molecular peak was observed, this compound has an 8.1 min retention time on HPLC (Buckychetler, toluene 4 mL/min). The desired product \(\Pi\) barely moved on the silica plate. By eluting with CH\(_3\)Cl, it moved with the solvent front. On HPLC the desired adduct has a \(t_r\) = 9.50 min (Buckychetler, toluene 4 mL/min). MALDI-TOF: \(m/z\) = 2125.81.

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