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Reactivity differences of Sc$_3$N@C$_{2n}$ (2n = 68 and 80). Synthesis of the first methanofullerene derivatives of Sc$_3$N@D$_{5h}$-C$_{80}$
Reactivity differences of $\text{Sc}_3\text{N}@\text{C}_{2n} (2n = 68 \text{ and } 80)$.

Synthesis of the first methanofullerene derivatives of $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$

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Using a purification method introduced earlier based on redox properties it was possible to isolate $\text{Sc}_3\text{N}@D_{3h}\text{-C}_{80}$ and $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{78}$ and a mixture of $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$ and $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{68}$. Taking advantage of their chemical reactivity differences, $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$ was isolated from $\text{Sc}_3\text{N}@D_{2h}\text{-C}_{68}$ followed by further functionalization, giving rise to five new methano-derivatives of $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$.

In 1999 Stevenson et al. reported the third most abundant fullerene that can be prepared in an arc reactor, $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$. The discovery of the trimetallic nitride endohedral fullerene (TNT) family includes the non-IPR $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$, the IPR $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{78}$ and the $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{68}$ isomer, all containing the same encapsulated triscandium nitride cluster inside.$^6$–$^9$

It is convenient that four different and interesting compounds are obtained in a single arcing experiment but their efficient separation presents many challenges. Several methods to isolate endohedral fullerenes have been reported,$^{10}$–$^{14}$ but none of them result in the efficient purification of $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$. Taking advantage of the differences in the oxidation/reduction potentials of the members of the $\text{Sc}_3\text{N}@D_{2n}\text{-C}_{2n}$ ($n = 34, 39, 40$) family, we recently reported a selective chemical oxidation method that allows the isolation of pure $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$ and $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{78}$, leaving a mixture of $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{68}$ and $\text{Sc}_3\text{N}@D_{6h}\text{-C}_{68}$.$^5$

Exohedral functionalization of endohedral fullerenes is essential to improve their solubilities and to explore their properties and potential applications.$^{16}$–$^{20}$ There are very few examples of derivatives of $\text{Sc}_3\text{N}@\text{C}_{68}$ and $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{68}$ partly because of their low synthetic yields and also due to the very large number of derivative isomers that can be obtained, which makes their purification and characterization very difficult. For example, the $D_3$ symmetric non-IPR $\text{Sc}_3\text{N}@\text{C}_{68}$ possesses 18 different types of bonds (Fig. 1), so an unsymmetric addend could yield 35 possible regioisomers.$^3$–$^9$ In the case of the $D_{3h}$ symmetric $\text{Sc}_3\text{N}@\text{C}_{80}$, which has higher symmetry, there are nine different types of bonds and 15 possible regioisomer derivatives (Fig. 1).$^4$–$^5$

There is only one example of an organic solar cell based on an endohedral fullerene acceptor (PCBH–Lu$_3$N@D$_{5h}\text{-C}_{68}$).$^{27}$ The main advantage of the endohedral fullerenes in photovoltaic applications results from their higher reduction potentials when compared to C$_{60}$ and C$_{70}$ (LUMO level),$^{28}$ that results in higher open circuit voltages ($V_{oc}$) and thus to higher power conversion efficiencies.

Here we report the separation of $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{68}$ from $\text{Sc}_3\text{N}@D_{6h}\text{-C}_{68}$ based on their chemical reactivity differences.$^{10}$–$^{20}$–$^{30}$

Exohedral functionalization of $\text{Sc}_3\text{N}@\text{C}_{68}$ was performed using a cyclopropanation reaction with the $p$-toluenesulfonyl tosyl hydrazone of phenyl butyric acid methyl ester to yield the corresponding PCBM-type derivatives. We also present for the first time the synthesis and characterization of five PCBM methano-derivatives of $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{68}$ (including the X-ray diffraction structure of one of the isomers) and two PCBM methano-derivatives of $\text{Sc}_3\text{N}@\text{C}_{68}$.

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Separation of Sc₃N@D₃h-C₆₈: a sample containing a mixture of Sc₃N@D₁₈h-C₆₈ and Sc₃N@C₆₈ was obtained as described previously, by the selective oxidative/reductive removal of Sc₃N@D₁₈h-C₆₈ and Sc₃N@C₇₈. Sc₃N@D₁₈h-C₆₈ was then isolated from Sc₃N@C₆₈ by using a chemical reaction with the p-toluenesulfonyl tosyl hydrazone of phenyl butyric acid methyl ester (Compound 1, Scheme 1). This reaction afforded new endohedral derivatives of Sc₃N@C₆₈ and also provided a convenient separation method to purify Sc₃N@D₃h-C₆₈.

The use of very accurate quantities of the reagents was crucial to successfully remove the Sc₃N@C₆₈ and isolate pure Sc₃N@D₃h-C₆₈. Once the isomeric compounds 2 and 3 in Scheme 1 (PCBM–Sc₃N@C₆₈) are formed, the pristine endohedral fullerene (Sc₃N@D₃h-C₆₈) can be easily separated from the reaction crude using regular silica gel column chromatography (Fig. S2, ESI†). To ensure the complete removal of Sc₃N@C₆₈, the reaction was followed by HPLC, taking an aliquot of the reaction crude and injecting it into the HPLC using a 5-PBB column. The optimized procedure employed 11.2 equivalents of tosyl hydrazone (Sc₃N@C₆₈, Scheme 1).31,32 This reaction afforded new endohedral derivatives of Sc₃N@C₆₈ and also provided a convenient separation method to purify Sc₃N@D₃h-C₆₈.

PCBM–Sc₃N@D₁₈h-C₆₈ to characterize the PCBM–Sc₃N@C₆₈ monoadducts the reaction was repeated with fewer equivalents of 1 to yield two main monoadduct isomers (2 and 3, Fig. 2). The two isomers were purified by HPLC and characterized by ¹H-NMR, mass spectrometry and UV-vis spectroscopy (Fig. S5–S11, ESI†). Although the D₃ symmetry of Sc₃N@C₆₈ can result in 35 possible regioisomers, we only observed two, which suggests a highly regioselective formation pathway, possibly directed by the encapsulated cluster inside.33,34

Sc₃N@D₁₈h-C₆₈ possesses eight different types of [6,6]-bonds, nine different types of [5,6]-bonds and one type of [5,5]-bond (Fig. 1a, Scheme 2). Due to the lack of symmetry of the addend used, with the spectroscopic evidences at hand, we cannot discard any of the 35 possible regioisomers for Sc₃N@D₁₈h-C₆₈.

Cyclopropanation reactions using hydrazones typically occur under thermodynamic control. Dorn and co-workers as well as Poblet and co-workers predicted that the main product under thermodynamic control for a Diels–Alder reaction, where it was predicted by Poblet and co-workers for a Diels–Alder reaction, where it was predicted by vide infra, addition to bond b-2 would be the preferred product. The second preferred isomer would be on either bond a- or bond b-. Comparable results were observed by Akasaka and co-workers for a Diels–Alder reaction, where it was predicted by

![Scheme 2 Different possible bonds on a fullerene.](image-url)

### Table 1 Relative energies for the lowest-energy PCBM monoadducts for Sc₃N@D₁₈h-C₆₈ and Sc₃N@D₃h-C₆₈ including solvent effects (o-dichlorobenzene)°

<table>
<thead>
<tr>
<th>Reacting bond</th>
<th>Bond type</th>
<th>E₉ (kcal mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>b-2*</td>
<td>[6,6]</td>
<td>Pyrene</td>
</tr>
<tr>
<td>b-3</td>
<td>[5,6]</td>
<td>Corannulene</td>
</tr>
<tr>
<td>b-4</td>
<td>[5,6]</td>
<td>Corannulene</td>
</tr>
<tr>
<td>b-5</td>
<td>[5,6]</td>
<td>Pyracylene</td>
</tr>
</tbody>
</table>

° Due to the non-symmetric addend, two different regioisomers are possible at each bond, with energy differences always within 1 kcal mol⁻¹ (see ESI). For those bonds that contain a symmetry element (denoted with an asterisk), only one possible regioisomer exists. ° Bonds are labelled without the prefix b- in Fig. 2.
DFT that bonds adjacent to the pentalene unit are chemically more reactive.

**PCBM–Sc₃N@D₅h-C₈₀**: the same PCBM reaction was performed using pure Sc₃N@D₅h-C₈₀ and compared to that reported for the I₅h-C₈₀ isomer. While Sc₃N@I₅h-C₈₀ yields only one PCBM derivative isomer, we observed five isomers for Sc₃N@D₅h-C₈₀, out of the 15 distinct possibilities (4, 5, 6, 7 and 8). The five isomers were purified by HPLC (Fig. 3) and characterized by NMR spectroscopy, mass spectrometry and UV-vis spectroscopy (Fig. S12–S25). Cyclic voltammetry (CV) was recorded for isomers 4, 6, 7 and 8 and the crystal structure was obtained for isomer 7.

Sc₃N@D₅h-C₈₀ possesses five different [6,6]-bonds and four different [5,6]-bonds (Fig. 1b, Scheme 2). Based on the available spectroscopic data it is not possible to discard any of the 15 possible regioisomers for Sc₃N@D₅h-C₈₀.

Unfortunately, we cannot compare our results with the monoaduct of Sc₃N@D₅h-C₈₀ synthesized via a 1,3-dipolar cycloaddition or to those calculated for the Diels-Alder additions, because it has been shown that for endohedral fullerene monoadducts different reaction types yield different regioisomers. For example, 1,3-dipolar cycloadditions on Sc₃N@I₅h-C₈₀ result in addition to [5,6]-bonds as the thermodynamic product, while cyclopropanation reactions typically result in additions to [6,6]-bonds with only one exception reported. For this reason we computed the lowest energy regioisomers using DFT. The results collected in Table 1 show that bond b-t leads to the thermodynamically preferred monoaduct, followed by bond b-c at 7.6 kcal mol⁻¹. Adducts on bonds b-b, -a and -t are between 8 and 9 kcal mol⁻¹ higher in energy; the remaining adducts are at more than 10 kcal mol⁻¹. Predicted molar fractions up to 400 K show that bond b-t leads to the most abundant adduct (see ESI†). These results are in full agreement with the X-ray structural determination of compound 7, vide infra. Therefore, we might infer that this type of addition is likely to take place under thermodynamic control. If this were the case, adducts on bonds b-c and -b could be the other observed isomers in the HPLC chromatogram (compounds 4, 5, 6 and 8; Fig. 1b and 3). However, we cannot completely discard adducts on bonds b-a and -t, which are very close in energy to adducts on bonds b-c and -b. A detailed study of the reaction paths, is beyond the scope of this work.

**Crystallographic results**: black, single crystals of 7-CS₂ were grown from a solution in CS₂, CDCl₃ and hexanes by slow diffusion. The structure of the compound is shown in Fig. 4. As the top drawing shows, the internal Sc₃N group, which is ordered, is oriented so that one of the scandium ions is located near the site of addition. The lower drawing, which omits the Sc₃Ng roof for clarity, shows the position of addition along the band of hexagons at the middle of the D₅h-C₈₀ cage. Adduct formation has resulted in the rupture of the bond that formerly connected C₃8 and C₄3 in the cage. The non-bonded C₃8···C₄3 distance in 7 is 2.20(2) Å, whereas in pristine Sc₃N@D₅h-C₈₀ the corresponding bonded C–C distance is 1.462 Å, which is the longest such distance in the cage. The redox properties were studied for isomers 4, 6, 7 and 8 of PCBM–Sc₃N@D₅h-C₈₀ using CV, with a scan rate of 100 mV s⁻¹ in o-DCB solutions and 0.05 M of n-Bu₄NPF₆ as supporting electrolyte. The CV results are summarized in Table S1, see ESI†. The cyclic voltammograms of isomers 4, 6, 7 and 8 showed three or four irreversible reduction waves, all cathodically shifted compared to those reported for the corresponding pristine fullerene Sc₃N@D₅h-C₈₀. These results are in agreement with previous reports of cathodic shifts upon double bond removal by chemical functionalization. Isomers 4, 6, 7 and 8 also showed two or four reversible oxidation waves cathodically shifted compared to those of the corresponding pristine fullerene (Fig. S14, S19, S22 and S25, see ESI†).
The CV results showed that PCBM methano-derivatives of the Sc₃N@D₅₋₃C₈₀ possess higher reduction potentials when compared to PC₆₁BM and PC₇₁BM (LUMO level), thus higher open circuit voltages (Vₒₜ₈) could be expected when used in organic photovoltaic solar cells. The CV of isomers 7 and 8 exhibited very similar reduction potentials to those reported for PCBH–Lu₃N@I₅₋₃C₈₀, thus if all other factors remain constant, similar open circuit voltages could be expected.

In conclusion, we report for the first time a convenient separation method of Sc₃N@D₅₋₃C₈₀ from Sc₃N@C₆₈ based on chemical reactivity differences, and the exohedral functionalization of the two members of the Sc₃N@C₂₉(n = 34 and 40) family, to yield the corresponding PCBM analogues. We also synthesized and characterized the first methano-derivatives of Sc₃N@D₅₋₃C₈₀ and the X-ray diffraction structure of one of the isomers. Using Sc₃N@C₆₈ and the PCBM-diazio precursor we predict preferential addition on the b=2 bond, the same regioisomer reported for the 1,3-dipolar cycloaddition and the Bingel reaction.

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Notes and references