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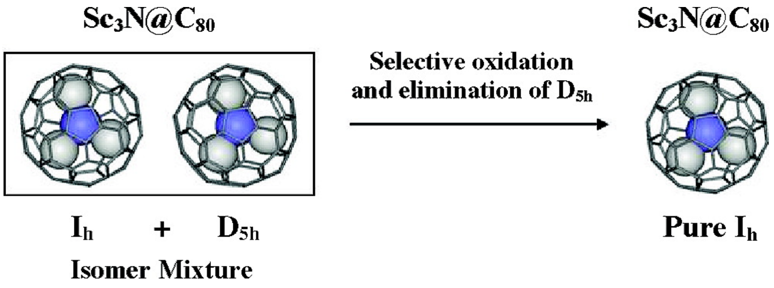

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# A Simple Isomeric Separation of $D_{5h}$ and $I_h$ $Sc_3N@C_{80}$ by Selective Chemical Oxidation

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***Abstract:*** Two electrochemical oxidation waves assigned to the $D_{5h}$ isomer of $Sc_3N@C_{80}$ have been identified, and a 270-mV difference in the first electrochemical oxidation potentials of the $I_h$ and $D_{5h}$ isomers has been measured. On the basis of this oxidative potential difference, a strategy for isomeric purification involving a selective chemical oxidation of the $D_{5h}$ isomer is reported. Variable scan cyclic voltammetry of the resultingly pure $Sc_3N@C_{80}$ $I_h$ isomer shows evidence of a rapid endohedral chemical reaction following the first reduction process.

## Introduction

Among the rather large family of endohedral metallofullerenes, the trimetallic nitride-containing fullerenes are unique because of their heteroatomic endohedral clusters. Because of their interesting electronic and structural properties, these molecules have been proposed as promising candidates for MRI contrast agents,[1−5] radiopharmaceuticals,[6−8] and electronic components.[9] The prototype of the family, $Sc_3N@C_{80}$, was first synthesized in 1999.[10] Although the icosohedral ($I_h$) isomer of $C_{80}$ is known to be the least thermodynamically stable of the seven possible empty-cage constitutional isomers due to its open-shell electronic ground state,[11] the prominent cage isomer of $Sc_3N@C_{80}$ was found to be $I_h$. Calculations had predicted that the icosohedral isomer of empty $C_{80}$ is greatly stabilized by the addition of six electrons,[12] and subsequent calculational[13] and experimental[14] studies revealed that the endohedral scandium nitride cluster formally transfers six electrons to the 4-fold degenerate HOMO (originally containing two unpaired electrons) on the carbon cage, forming an electronically closed-shell ground state. A more recent article has revealed the existence of another isomer of $Sc_3N@C_{80}$.[15] This $D_{5h}$ symmetry isomer was less abundant, constituting approximately 10% of the entire fullerene sample.

In 2004, Krause and Dunsch reported the first separation of two isomers of $Sc_3N@C_{80}$, which they identified as having $I_h$ and $D_{5h}$ symmetry.[16] The $D_{5h}$ isomer in this study was also found to be the minor component (~15−20%), eluting just after the $I_h$ isomer as a shoulder on the more prominent HPLC peak. The isomeric separation was achieved using a linear combination of two analytical HPLC columns, and the isolated isomers were studied using various spectroscopic methods. The $I_h$ fraction was also examined by cyclic voltammetry (CV), revealing two quasi-reversible reductions and one oxidation.

In this article, a technique for separating the two isomers of $Sc_3N@C_{80}$ by selective chemical oxidation of the $D_{5h}$ isomer is reported. From an isomeric mixture, this method yields pure icosohedral $Sc_3N@C_{80}$ after a single oxidative step and can be scaled to any amount. Although both selective electrochemical reduction[17] and chemical oxidation[18] have been used to solubilize and separate different endohedral metallofullerenes, to our knowledge this is the first reported isomeric fullerene purification utilizing differences in redox potentials as the basis for the separation. In addition, we report here a variable scan rate voltammetric study of $I_h$ $Sc_3N@C_{80}$ suggesting that, upon reduction, the endohedral $Sc_3N$ cluster undergoes a rapid geometric and/or electronic change resembling a chemically irreversible reaction.

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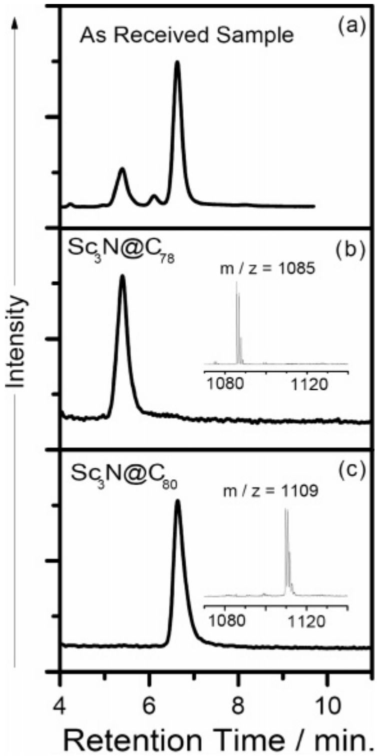

***Figure 1.*** HPLC chromatograms of (a) as-received Sc$_3$N@C$_{2n}$ ($n$ = 39, 40) from Luna, (b) the first major fraction, and (c) the isomeric mixture of Sc$_3$N@C$_{80}$. The insets show the MALDI-TOF mass spectrum of the two chromatographically pure fractions.

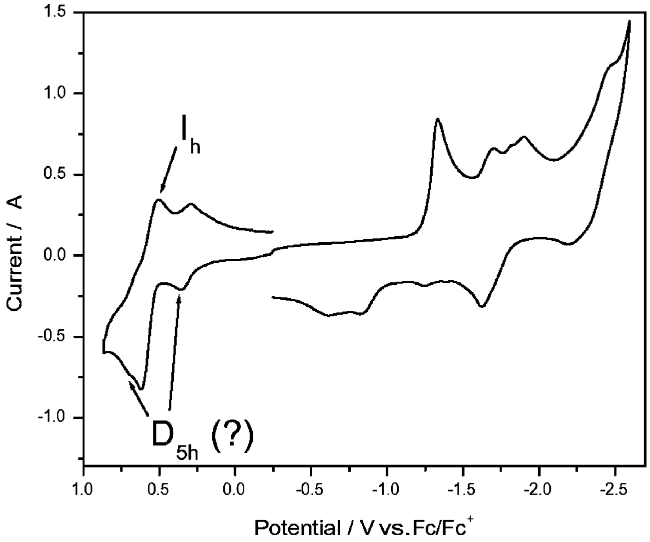

***Figure 2.*** Cyclic voltammogram of the isomeric mixture of Sc$_3$N@C$_{80}$ in *o*-dichlorobenzene, 0.1 M TBAPF$_6^-$, 100 mV/s scan rate. Arrows indicate oxidation waves of each isomer.

## Results and Discussion

HPLC analysis of Sc$_3$N@C$_{2n}$ ($n$ = 39, 40) samples obtained from Luna Innovations, Inc. showed three prominent peaks (Figure 1). HPLC chromatographic separation and subsequent MALDI-TOF MS analysis revealed that the first peak was Sc$_3$N@C$_{78}$, and the third largest peak was Sc$_3$N@C$_{80}$. In the isomer separation process described by Krause and Dunsch, two consecutive analytical Buckyprep columns were utilized, and both the $I_h$ and $D_{5h}$ isomers were observable by HPLC, the $D_{5h}$ as a trailing shoulder on the larger $I_h$ peak. The HPLC experiments described here were carried out with a Buckyclutcher semipreparative column, which did not allow the separation of the two isomers chromatographically. The largest peak, corresponding to the Sc$_3$N@C$_{80}$ isomer mixture, was isolated by HPLC using the Buckyclutcher column (Figure 1c), thus eliminating Sc$_3$N@C$_{78}$ and the middle peak observed in Figure 1a. The identity of this middle peak remains unknown at the present time.

Cyclic voltammetry of the chromatographically pure Sc$_3$N@C$_{80}$ fraction (presumably containing both $I_h$ and $D_{5h}$ isomers) was performed in *o*-dichlorobenzene (Figure 2). At normal scan rates, the reductive waves of the voltammogram were chemically irreversible, unlike the voltammetry reported by Krause and Dunsch. In addition, the oxidative side of the Sc$_3$N@C$_{80}$ voltammogram contained two additional smaller waves: the first, 270 mV less positive, and the second, 80 mV more positive than the one previously reported for the $I_h$ endohedral isomer.[16] Since MALDI-TOF showed only a single mass for this chromatographically pure sample, we posited that the smaller oxidation waves, having relative intensities of approximately 1:3, were caused by the less abundant $D_{5h}$ isomer present in the sample, as shown in Figure 2. Fullerene isomers with such drastically different oxidation potentials are known.[19] For example, the $C_{2v}$ and $D_3$ isomers of C$_{78}$ were found to have first and second oxidation potentials 250 and 260 mV apart with peak intensities of 5:1, in agreement with the experimentally determined isomeric ratio.[20] The less abundant C$_{78}$ $D_3$ isomer was easier to oxidize than the major $C_{2v}$ isomer,[21] in agreement with calculated HOMO−LUMO energies.[22] Four different isomers of C$_{84}$ have also been shown to exhibit first oxidations at various potentials, although with a much lower spread (20−50 mV potential difference).[23] Additional evidence for the tentative Sc$_3$N@C$_{80}$ $D_{5h}$ assignment is provided by a theoretical study by Nakao et al., who calculated a much smaller HOMO−LUMO gap for the $D_{5h}$ isomer of C$_{80}^{6-}$ than for the $I_h$ hexaanion.[24] From the lowest energetic absorptions of NIR experimental data, Krause and Dunsch also assigned a lower optical gap energy to the $D_{5h}$ isomer of Sc$_3$N@C$_{80}$.[16]

Although the Buckyclutcher HPLC column could not resolve the two Sc$_3$N@C$_{80}$ isomers, their different electrochemical behavior suggested an alternate separation technique based on their oxidative reactivity differences. Since the first oxidation wave in the Sc$_3$N@C$_{80}$ voltammogram was considerably less positive than the potential of the first icosohedral oxidation (Figure 2), a suitable chemical oxidant with an oxidation potential falling between the first two oxidation waves was selected. Reacting the isomeric mixture with this oxidant should preferentially oxidize the $D_{5h}$ isomer and enable a separation based on charge. The oxidant used was tris(*p*-bromophenyl)-aminium hexachloroantimonate (TPBAH). This cation radical salt has an oxidation potential between the first oxidations of the $I_h$ and $D_{5h}$ isomers and is soluble in *o*-dichlorobenzene. Reacting TPBAH in a 2:1 excess with the Sc$_3$N@C$_{80}$ isomer

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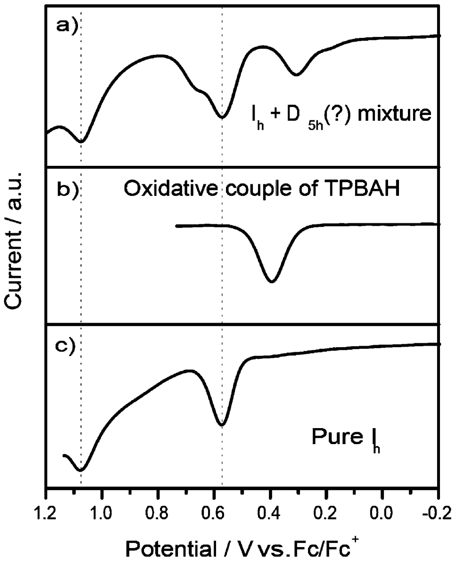

***Figure 3.*** OSWV of (a) the $I_h$ and $D_{5h}$ $Sc_3N@C_{80}$ isomer mixture, (b) the oxidation wave of the neutral amine oxidant precursor, and (c) pure icosohedral $Sc_3N@C_{80}$.

mixture in solution, previously separated from $Sc_3N@C_{78}$ by HPLC, followed by deposition of the reaction mixture onto the top of a silica column resulted in the quantitative removal of $D_{5h}$ $(Sc_3N@C_{80})^{\bullet +}$. The unoxidized $I_h$ isomer was separated from the tris(*p*-bromophenyl)amine by elution with $CS_2$, while the cation radical of the $D_{5h}$ isomer remained adsorbed on the silica. Any excess unreacted oxidation agent was also adsorbed. After the separation, MALDI-TOF showed a parent peak indicative of $Sc_3N@C_{80}$, and Osteryoung square wave voltammetry (OSWV) clearly showed the absence of the two oxidations previously assigned to the $D_{5h}$ isomer (Figure 3). Further work is in progress to attempt the recovery of the $D_{5h}$ isomer as well.

After separation of the $I_h$ isomer from the $D_{5h}$ $Sc_3N@C_{80}$ and from $Sc_3N@C_{78}$, it was still evident that its reductive electrochemistry remained irreversible. In an effort to address this distinct irreversibility, attention was focused on the first reduction wave. At a scan rate of 100 mV/s, the first reduction is irreversible, with a broad and anodically shifted reoxidation. Our platinum disk working electrode was exchanged for both gold and glassy carbon working electrodes with no resulting change in the appearance of the first reduction wave, suggesting that the observations are not due to surface adsorption/desorption. Changing the $Sc_3N@C_{80}$ solution concentration also made no difference in the electrochemical reversibility. To probe the kinetics of the first anion formation, cyclic voltammetry at various scan rates was performed. Scan rates slower than 100 mV did not significantly change the appearance of the first reduction wave, but increasing the scan rate incrementally caused it to become more chemically reversible. Figure 4 shows the scan rate dependence on the reversibility of the first reduction wave. At extremely high scan rates, the anodically shifted reoxidation disappears, and the first reduction wave becomes reversible. In fact, if the potential window accessible on the reductive side of the electrochemistry is scanned fast enough, all the small features disappear, and three reversible waves with spacing suggestive of a nondegenerate LUMO and accessible LUMO+1 constitute the reductive voltammogram (Figure 5). (The two oxidations of the $I_h$ isomer, unlike the reductive waves, were both quasi-reversible at a normal 100 mV/s scan rate.)

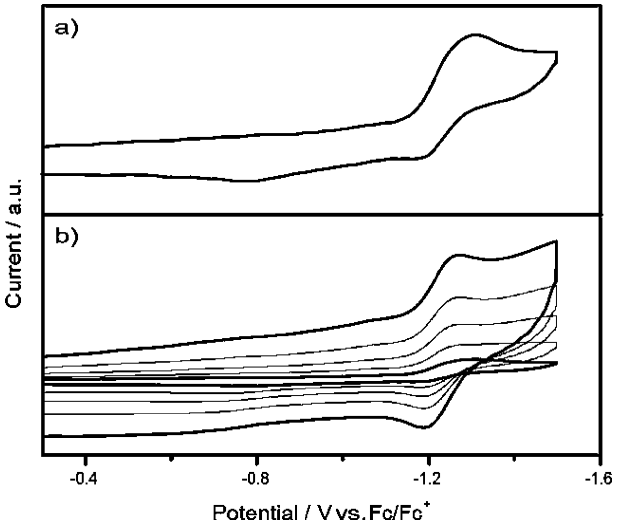

***Figure 4.*** CV scan rate study of the first reduction wave of pure icosohedral $Sc_3N@C_{80}$ at scan rates of (a) 100 mV/s and (b) 100, 400, 1000, 2000, 4000 mV/s. The two separate voltammograms are not shown to scale.

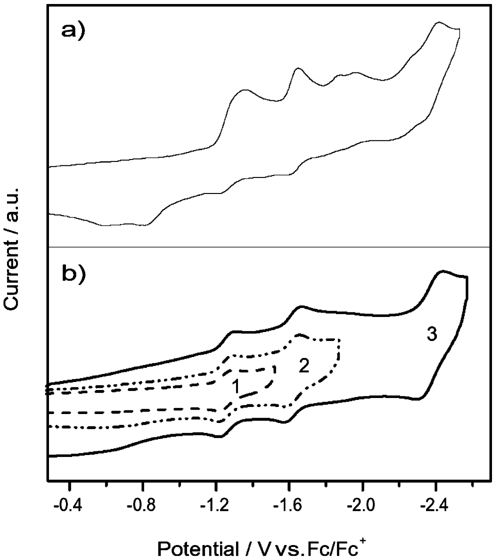

***Figure 5.*** CV of the reductions of pure icosohedral $Sc_3N@C_{80}$ at scan rates of (a) 100 mV/s, and (b) 6 V/s (1), 10 V/s (2), and 20 V/s (3). The different scan rates for each reduction reflect the speed necessary for achieving full electrochemical reversibility.

***Table 1.*** Electrochemical Redox Potentials, V versus Fc/Fc$^+$ (ODCB)

| | $E^{2+/1+}$ | $E^{1+/0}$ | $E^{0/1-}$ | $E^{1-/2-}$ | $E^{2-/3-}$ |
|---|---|---|---|---|---|
| $Sc_3N@C_{80}$ ($I_h$) | 1.09 | 0.59 | −1.26 | −1.62 | −2.37 |
| $Sc_3N@C_{80}$ ($I_h$)[a] | | 0.62 | −1.24 | −1.62 | |
| $C_{60}$ | | 1.33 | −1.15 | −1.55 | −2.01 |

[a] Reference 16.

Table 1 shows the measured oxidation and reduction potentials of $Sc_3N@C_{80}$ in ODCB, along with those of Krause and Dunsch and of $C_{60}$ for comparison. Increased reversibility of the reductive waves at comparatively lower scan rates was also achieved by cooling the solution from room temperature to −10 °C. This scan rate- and temperature-dependent behavior is clear evidence that the electrochemical reduction is followed by a rapid chemical reaction (EC mechanism). If the anions formed by electrochemical reduction can be reoxidized quickly enough, the following chemical reaction is inhibited, and the electrochemistry becomes reversible. This “freezing” of the chemical reaction upon reduction can be achieved by either fast scans or low temperatures, which slow the reaction kinetics.

All evidence points to this rapid chemical reaction having an endohedral origin. It is well-known that reductions resulting in electron spin on the outside fullerene surface, as occur for most empty and endohedral fullerenes, are electrochemically and chemically reversible at normal scan rates. Of course, our electrochemical experiments with $Sc_3N@C_{80}$ have shown drastically different behavior. Both calculational[25] and experimental electron paramagnetic resonance (EPR)[26] studies of the $Sc_3N@C_{80}$ anion indicate that there is significant unpaired electron spin on the endohedral cluster due to its large electron affinity. Though the anion radical in the published EPR study was generated chemically, we have also generated the anion in our lab via controlled potential bulk electrolysis and duplicated the published 22-line EPR hyperfine pattern indicative of unpaired electron spin on three equivalent scandium atoms.[27] Upon reoxidation of the solution, we found the $Sc_3N@C_{80}$ sample unchanged, and we subsequently reused it for multiple electrolysis experiments. Therefore, the electrochemical behavior of at least the first reduction, and possibly the rest of the accessible reductions, is caused by an as-yet-unidentified change in the geometry, electronic structure, or bonding of the endohedral cluster, not by an exohedral reaction.

It is interesting to speculate on the nature of the cluster change upon addition of an electron based on current knowledge of the $Sc_3N$ unit’s behavior inside the $C_{80}$ cage. Although both calculational studies[25,28] and $^{13}C$ NMR data[10] point to unhindered cluster rotation in the neutral molecule at least on an NMR time scale, solid spectroscopic evidence of cluster-cage bond formation on a much shorter vibrational time scale exists.[29] The addition of an electron to the cluster could change the electrostatic interaction between the cluster and the cage and, thus, the rapid bonding that is characteristic of the neutral molecule. Another possibility is a reduction in the bond order of the cluster. Though EPR spectroscopy of the anion at room temperature has indicated equally shared electron spin on all three scandium atoms, it is possible that N−Sc bonds are breaking and re-forming on a shorter time scale than can be probed with this technique. Perhaps variable-temperature EPR and Raman spectroscopic studies of the $Sc_3N@C_{80}$ anion can identify the type of reaction that our electrochemical study has revealed. Such studies are currently underway in our lab.

## Experimental Section

HPLC purity analyses and separations were carried out using a Varian Pro Star model 320 and a semi-preparative 25 cm × 10.0 mm Buckyclutcher column. The eluent was toluene, and the flow rate was 4 mL/min. MALDI-TOF mass spectra were collected using a Bruker Omni Flex. All CV and OSWV experiments were carried out in a formal one-compartment cell in a solution of *o*-dichlorobenzene containing 0.1 M $(t\text{-Bu})_4NPF_6$ using a standard three electrode arrangement. A Pt disk (1 mm) was used as the working electrode, a Pt wire as the auxiliary, and a Ag wire in a 0.01 M $AgNO_3$/0.1 M $(t\text{-Bu})_4NPF_6$ $CH_3CN$ solution as the reference electrode. Ferrocene was added to the solution at the end of each experiment to act as an internal reference, and all electrochemical potentials were referenced to its redox couple. For bulk electrolysis, each experiment was carried out in a two-compartment cell with platinum gauze working and counter electrodes. After electrolysis, the solution was transferred to a quartz EPR tube, and first-derivative X-band spectra were recorded using a Bruker EMX spectrometer. The $Sc_3N@C_{80}$ solution concentrations ranged from $4 \times 10^{-4}$ to $8 \times 10^{-4}$ M in all cases, and a CHI 660A potentiostat controlled by a PC was used for all electrochemical measurements.

A typical chemical oxidative isomeric purification was carried out as follows: Two milligrams of the isomeric mixture of $Sc_3N@C_{80}$ was dissolved in 4 mL of *o*-dichlorobenzene. A 2:1 molar excess (to ensure complete oxidation of the $D_{5h}$ isomer) of TPBAH (Acros, 95%) was added to the fullerene solution and swirled until completely dissolved. This solution was placed on top of a silica column and eluted with $CS_2$ to separate the neutral $I_h$ isomer (brown, on solvent front) from the neutral reacted amine (colorless, just behind the fullerene band). Any charged species, such as the $D_{5h}$ isomer and the unreacted aminium salt, remained at the top of the column. The fractions containing only $Sc_3N@C_{80}$ were combined and evaporated. Typical yields were 50−60 wt % and did not change with varying starting amounts of the isomeric mixture.

## Conclusions

An isomeric separation process based on oxidation potential differences between the $I_h$ and $D_{5h}$ isomers of $Sc_3N@C_{80}$ is reported. The process is quick and easy and can theoretically be scaled up to any amount. A variable scan rate CV study of the $Sc_3N@C_{80}$ isomer with $I_h$ symmetry was also carried out, revealing a rapid endohedral chemical reaction immediately following the first reduction of the molecule.

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**Supporting Information Available:** EPR spectrum of the $Sc_3N@C_{80}$ anion radical. This material is available free of charge via the Internet at http://pubs.acs.org.

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