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Rapid Removal of D_{5h} Isomer Using the “Stir and Filter Approach” and Isolation of Large Quantities of Isomerically Pure $Sc_3N@C_{80}$ Metallic Nitride Fullerenes

Steven Stevenson,^{*,†} Mary A. Mackey,[†] Curtis E. Coumbe,[†] J. Paige Phillips,[†] Bevan Elliott,[‡] and Luis Echegoyen[‡]

Department of Chemistry and Biochemistry, University of Southern Mississippi, Hattiesburg, Mississippi 39406, and Department of Chemistry, Clemson University, Clemson, South Carolina 29634

Received February 3, 2007; E-mail: steven.stevenson@usm.edu

Metallic nitride fullerenes (MNFs) are metallofullerenes with entrapped inorganic clusters.¹ These molecules consist of a four-atom trimetallic nitride cluster trapped inside a fullerene cage. A major hurdle to MNF experimentation is the poor availability of isomerically pure samples. This paucity of material is due to inefficient separation technologies.

Typical soot extracts from scandium-doped graphite rods contain the dominant empty-cage fullerenes (e.g., >90%, C_{60} , C_{70}) and a mixture of $Sc_3N@C_{80}$ I_h and D_{5h} structural isomers. Historically, the $Sc_3N@C_{80}$ mixture of isomers has been separated by HPLC,^{2,3} a tedious process, due in part, to their similar retention times. Advances in nonchromatographic techniques have included selective chemical oxidation⁴ and chemical separation methods using a reactive cyclopentadienyl (CPD) resin^{5,6} or aminosilica⁷ to immobilize fullerene contaminants on solid supports.

In this Communication, we report a rapid, nonoxidative, non-chromatographic method for the rapid removal of this contaminant D_{5h} isomer. Using a reactive diamino silica with the “stir and filter approach” (SAFA),⁷ we compare the reactivity of the D_{5h} isomer relative to the I_h $Sc_3N@C_{80}$ isomer and empty-cage fullerenes. Results indicate a reactivity of C_{70} , C_{60} , and D_{5h} $Sc_3N@C_{80}$ > I_h $Sc_3N@C_{80}$. Of note is the rapid (13 h) removal of D_{5h} isomer using SAFA with diamino silica. This quick removal of D_{5h} isomer is significantly shorter than the longer 2–3 week reaction time described in the CPD-resin chemical separation approach.⁶

To demonstrate the difficulty of HPLC separations for I_h and D_{5h} $Sc_3N@C_{80}$ isomers, Figure 1 indicates elution differences of only 92 and 95 min, respectively. There is a clear lack of baseline resolution as the D_{5h} peak is a tail of the I_h elution. To assess, for the first time, the selectivity of the D_{5h} and I_h $Sc_3N@C_{80}$ isomers with reactive aminosilica, a SAFA experiment was performed using diamino silica. The objective was to monitor the reactivity differences between the I_h and D_{5h} $Sc_3N@C_{80}$ isomers.

For this SAFA experiment, 1.1 grams of Sc fullerene extract was dissolved in *o*-xylene, and 234 g of diaminosilica was added. The slurry was stirred, and aliquots were removed for HPLC analysis of I_h and D_{5h} $Sc_3N@C_{80}$ isomer content. At $t = 0$, the extract solution contained a 72% I_h and 28% D_{5h} $Sc_3N@C_{80}$ isomer mixture. After only 1 h of stirring, the SAFA reaction reduced the D_{5h} content from 28% to 9%, a 3-fold decrease (Figure 2). After 4 and 8 h of SAFA reaction time, the D_{5h} content

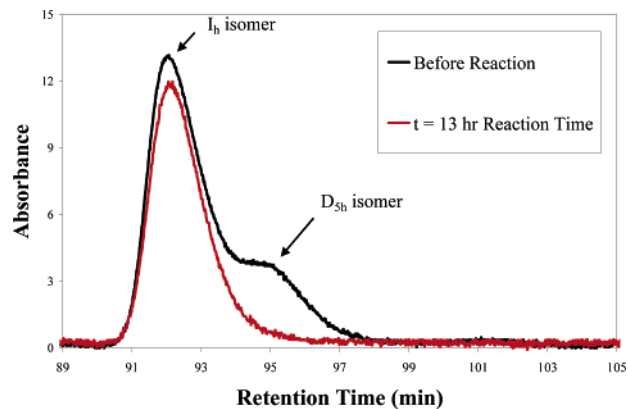


Figure 1. Chromatogram of scandium-containing fullerene extract before and after 13 h of SAFA reaction with aminosilica. HPLC conditions are 1.0 mL/min toluene, 360 nm UV, 50 μ L injection, and PYE column.

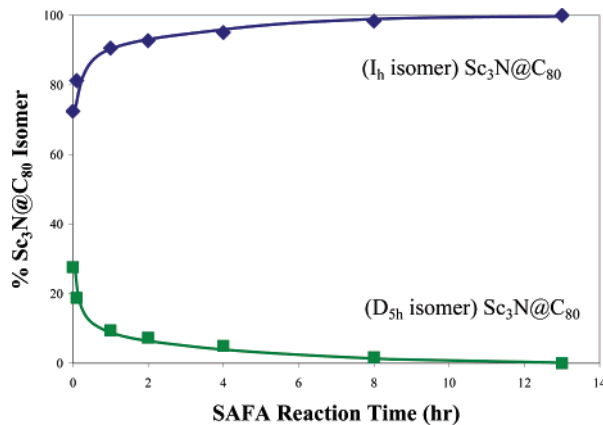


Figure 2. Percentages of I_h and D_{5h} $Sc_3N@C_{80}$ isomers at various SAFA reaction times with diaminosilica.

was further reduced to 5% and 1.5% abundance, respectively. After 13 h, the D_{5h} isomer was transferred from solution to the reactive silica.

In addition to the D_{5h} $Sc_3N@C_{80}$ isomer, empty-cage fullerenes (e.g., C_{70} , C_{76} , C_{78} , C_{84}) have also been removed from the solution and immobilized onto the diamino silica. The composition of the 13 h aliquot is $Sc_3N@C_{80}$ I_h (64%) and C_{60} (30%), with traces of $Sc_3N@C_{68}$ (2%) and $Sc_3N@C_{78}$ (4%) MNFs.

Further SAFA reaction time was required to fully remove C_{60} (1.5 days), and $Sc_3N@C_{68}$ and $Sc_3N@C_{78}$ (3.5 days). A summary of these results is shown in Figure 3.

[†] University of Southern Mississippi.

[‡] Clemson University.

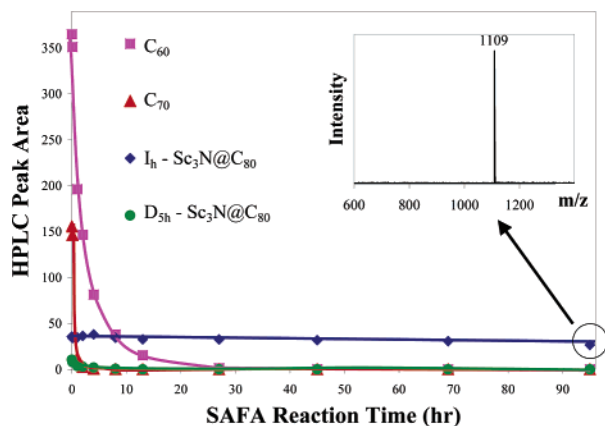


Figure 3. Overview of fullerene quantity remaining in solution with respect to reaction time; (inset) MALDI-TOF mass spectrum of SAFA purified I_h $Sc_3N@C_{80}$ isomer.

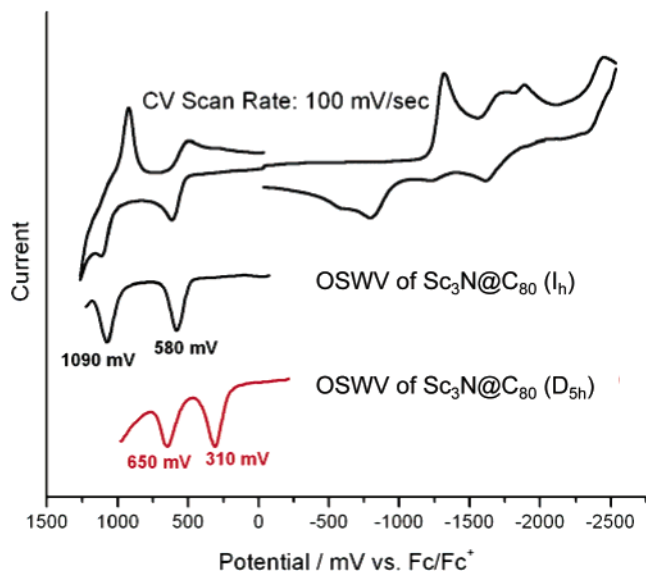


Figure 4. CV and OSWV electrochemical analysis of SAFA purified I_h $Sc_3N@C_{80}$ isomer.

Upon reaction completion, the slurry was filtered and washed, and the solvent was removed. From the SAFA technique, 0.112 g

of $Sc_3N@C_{80}$ was obtained. This sample was analyzed by mass spectrometry. MALDI-TOF data (Figure 3) indicate a sample with a fullerene purity of 99+% $Sc_3N@C_{80}$. Although HPLC data (Figures 1 and 2) demonstrate removal of D_{5h} isomer, further electrochemical analysis on this sample also confirms I_h isomeric purity for $Sc_3N@C_{80}$.

Specifically, cyclic voltammetry and Osteryoung square-wave voltammetry was performed (Figure 4) on this SAFA purified sample. OSWV data indicate oxidations for this I_h isomerically purified sample at 580 and 1090 mV. These oxidation potentials are consistent with previous literature values for I_h $Sc_3N@C_{80}$.⁴ Note the absence of D_{5h} oxidations, which would have been observed at 310 and 650 mV, if present.

In summary, the SAFA process with diamino silica rapidly removes the D_{5h} contaminant $Sc_3N@C_{80}$ isomer. We also report, for the first time, purification of large quantities (>100 mg) of isomerically pure I_h $Sc_3N@C_{80}$ as confirmed by sensitive analytical techniques such as electrochemistry.

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Supporting Information Available: HPLC data for initial extract. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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