

Purification of Trimetallic Nitride Templated Endohedral Metallofullerenes by a Chemical Reaction of Congeners with Eutectic 9-Methylanthracene

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The availability of pure samples is a major hurdle in the study of trimetallic nitride templated endohedral metallofullerenes (TNT EMFs). Current HPLC methods of purification are costly, nonrecyclable, and take considerable time. Reported herein is a solvent-free reaction of crude soot extract (empty-cage and Sc or Lu TNT EMFs) in molten 9-methylanthracene that affords almost complete conversion of empty-cage fullerenes to 9-methylanthracene adducts, while leaving TNT EMFs unreacted. After the recovered extract is washed with diethyl ether, the washed extract can then be applied to a silica gel column and subsequently flushed with toluene. To illustrate for Sc₃N@C₈₀, the sample was purified to ~60% in a time period of <24 h. Final one-step HPLC purification provided high-purity TNT EMF samples (>99%) in an expeditious and less costly manner.

Introduction

Since the inception of fullerene science, endohedral metallofullerenes have attracted attention due to the unique properties that result from the encapsulation of metal atoms inside the carbon cage.^{1,2} In particular, trimetallic nitride templated endohedral metallofullerenes (TNT EMFs)³ are considered one of the most important fullerene-based families of materials due to their abundance and diversity (e.g., various metals, cage sizes, and symmetries).^{4–11} The diversity of TNT EMFs coupled with the interesting properties of metals surrounded by an organic cage makes them potentially

useful for a wide variety of applications, for example, MRI contrast agents.¹²

To date, inadequate availability of pure endohedral metallofullerenes has hindered research on these new nanomaterials. Although the trimetallic nitride template method of fullerene production can afford macroscopic quantities of materials such as Sc₃N@C₈₀,³ the mixed fullerenes created in a Krätchmer–Huffman electric arc generator are still dominated by empty-cage fullerenes (e.g., C₆₀, C₇₀, etc.), and considerable purification is necessary. Traditionally, endohedral metallofullerenes have been isolated by multistep liquid chromatographic methods.^{13–15} However, the poor solubility of endohedral metallofullerenes limits the sample loading; thus, it is very time and solvent intensive to obtain them in macroscopic quantities. Alternatively, chemical separations recently were used to isolate TNT EMFs. Two such methods have been reported so far: the selective binding of empty-cage fullerenes to cyclopentadiene-functionalized Merrifield resin¹⁶ and a similar reaction with amino-capped silica gel.¹⁷

While these two chemical separation methods differ in mechanism, the principle as to how they work is the same.

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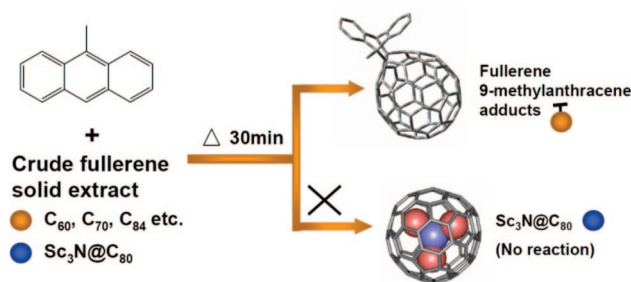
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C₆₀ and other empty-cage fullerenes are electron deficient olefins and therefore are fairly reactive species in many reactions, such as cycloadditions. However, theoretical calculations demonstrate that TNT EMFs are stabilized by the transfer of six electrons from the internal trimetallic nitride (A₃N) cluster to the carbon cage, resulting in a closed shell electronic structure and a large energy gap.^{18–24} The lower reactivity of TNT EMFs relative to empty-cage fullerenes in cycloadditions has been demonstrated: functionalization of TMFs requires more severe reaction conditions (i.e., elevated temperatures and/or large reagent excesses) than similar reactions with empty-cage fullerenes.^{25–27}

The support-based purification methods noted previously are effective at yielding TNT EMF samples of >98% purity; however, both methods are fairly expensive and time-consuming (requiring a minimum of 2 days to achieve effective separation). Also, neither method has been demonstrated to completely release the reacted fullerenes from the support and thus be completely recyclable. Seeking to reduce the amount of time and the cost of obtaining pure TNT EMFs, we believe a support-free method of isolation would be an effective alternative. In this case, a support-free separation method would theoretically take less time by eliminating the time to synthesize the support and avoiding lengthy reaction/elution times. An ideal support-free separation method also would reduce cost by being fully reversible and recyclable. Many studies on Diels–Alder reactions and retro-reactions of C₆₀ with acenes have been reported.^{28–32} Saunders and co-workers also reported the separation of C₈₄ isomers by using the reversible Diels–Alder reaction of C₈₄ with 9,10-dimethylanthracene.³³ A similar isolation procedure for C₆₀ from a C₆₀–C₇₀ mixture was reported by Wang and co-workers.³⁴ Kräutler and co-workers found that the most efficient method of forming Diels–Alder adducts with anthracene and C₆₀ is to perform a solvent-

Scheme 1. Reaction of Fullerene Extracts with 9-Methylantracene



free reaction in which the reaction mixture is heated above the melting point of the anthracene.^{30,35}

Using a variation of Kräutler's solvent-free method of forming anthracene–C₆₀ adducts (Scheme 1), we herein discuss the reaction of a large excess of a low-melting anthracene (9-methylantracene) with Sc- and Lu-based soot extracts and the separation of the reacted empty-cage fullerenes from the unreacted TNT EMFs.

Experimental Procedures

Materials and Methods. Graphite rods (99.9995% C, 12.7 mm × 152 mm) and graphite powder (99.9995% C) were obtained from Alfa Aesar. The graphite rods were drilled longitudinally to provide a 5/16 in. (8 mm) hole, which was packed with the metal oxide, Fe_xN, and graphite powder; the latter three components were mixed with a mortar and pestle, and the graphite rod was packed with the resultant mixture placed in the rod and tamped down with the blunt end of the 5/16 in. drill bit. Scandium (III) oxide (Sc₂O₃, 99.999%) and lutetium (III) oxide (Lu₂O₃, 99.995%) were obtained from Stanford Materials Corporation. Iron nitride (99.9%, Fe_xN, *x* = 2–4) and 9-methylantracene (99%) were obtained from Alfa Aesar. Anhydrous diethyl ether was obtained from Fisher Scientific. A β-(1-pyrenyl)ethyl silica (PYE) column (10 mm × 250 mm, Alltech Associates) was used in high-pressure liquid chromatography (HPLC) for both analysis and purification.

Sc₃N@C₈₀-Containing Soot Extract. Sc₃N@C₈₀ was prepared by arc-vaporization of graphite rods packed with Sc₂O₃ (4.9 g, 35.5 mmol), Fe_xN (0.28 g), and graphite powder (1.82 g, total carbon ~12.5 g) in a K–H generator under a dynamic N₂ (33 mL/min)/He (545 mL/min) atmosphere (at 300 Torr total pressure). The graphite rods were typically baked at ~1025 °C under N₂ for 8 h and allowed to cool under N₂ just prior to arc-vaporization. A potential difference of 27 V was applied between the ends of the rods and maintained via electronic control. After each rod had been consumed (~60 min), the resulting soot was collected. The soot from 10 rods was combined and placed in a Soxhlet extractor with *o*-xylene for 18 h to obtain 1.2 g of soot extract (mixed fullerenes and metallofullerenes).

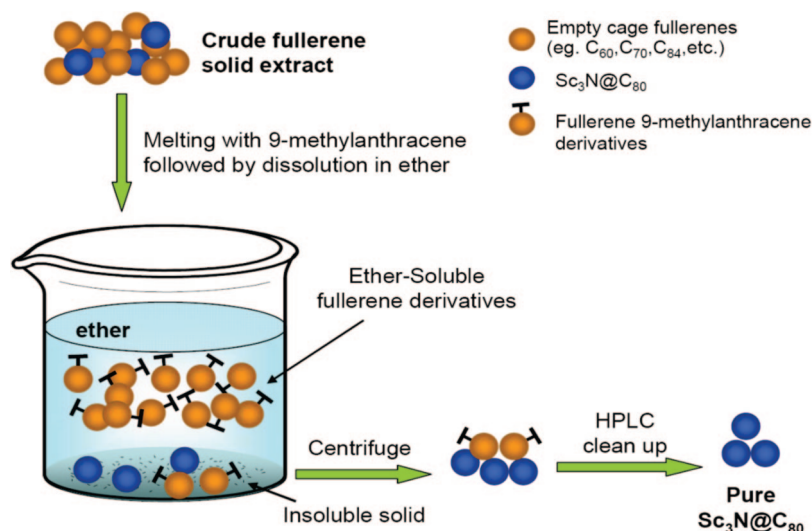
Lu₃N@C₈₀-Containing Soot Extract. Lu₃N@C₈₀ was prepared from graphite rods packed with Lu₂O₃ (7.68 g 19.3 mmol), Fe_xN (0.48 g), and graphite powder (3.84 g, total carbon ~14.84 g). The soot from 28 rods was combined and subjected to Soxhlet extraction with *o*-xylene for 18 h to obtain 2.3 g of soot extract (mixed fullerenes and metallofullerenes).

Purification of Sc₃N@C₈₀ from Soot Extract. The extract was rinsed with diethyl ether to render it powdery, and 25 mg (35 μmol assuming all was C₆₀) was mixed with 125 mg (0.651 mmol) of

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Scheme 2. Schematic of Isolation of $\text{Sc}_3\text{N}@C_{80}$ from Empty-Cage Fullerenes by Reaction with 9-Methylantracene, a Support-Free Method



9-methylantracene in a 13 mm \times 100 mm test tube. The mixture was placed in an oil bath at 140–145 $^{\circ}\text{C}$ and heated for 30 min, followed by cooling under tap water. The resulting black solid was pulverized, placed in \sim 40 mL of diethyl ether, sonicated for 10 s, and centrifuged, and the supernatant was removed with a pipet; the washing process was performed a total of 6 times. The ether-insoluble solid TNT EMF-enriched sample (7 mg) was subsequently dissolved in toluene. In the final stage, HPLC was utilized to provide 2 mg of high-purity ($>99\%$) $\text{Sc}_3\text{N}@C_{80}$.

Purification of $\text{Lu}_3\text{N}@C_{80}$ from Soot Extract. The Lu soot extract was treated identically to the Sc soot extract.

Enrichment of $\text{Sc}_3\text{N}@C_{80}$ by Column Chromatography. A 10 mg extract sample of scandium soot was mixed with 50 mg of 9-methylantracene in a 13 mm \times 100 mm test tube and heated at 140–145 $^{\circ}\text{C}$ for 30 min, followed by cooling under tap water. The resulting black solid was pulverized, placed in \sim 40 mL of diethyl ether, sonicated for 10 s, and centrifuged, and the supernatant was removed with a pipet; the washing process was performed a total of 3 times. The ether-insoluble solid TNT EMF-enriched sample was applied to a glass column (22 mm \times 300 mm) packed with 35 g of 200–400 mesh silica gel. The column was initially flushed with diethyl ether/toluene (3:7 v:v) until the first fraction eluted from the column. The first fraction consisted of mainly empty-cage 9-methylantracene adducts as well as $\sim 10\%$ $\text{Sc}_3\text{N}@C_{80}$ (~ 0.5 h). The second fraction was collected when the column was subsequently eluted with 100% toluene. The percentage of $\text{Sc}_3\text{N}@C_{80}$ in the second fraction increased to 60% purity.

Results and Discussion

The overall approach is illustrated in Scheme 2. HPLC chromatograms of the soot extract are shown at each step in the process for $\text{Sc}_3\text{N}@C_{80}$ (Figure 1). After being mixed and heated with an excess of 9-methylantracene at 140–145 $^{\circ}\text{C}$ for 30 min, all of the fullerenes in the soot extract were derivatized except $\text{Sc}_3\text{N}@C_{80}$ and small amounts of C_{60} , C_{70} , C_{84} , and $\text{Sc}_3\text{N}@C_{78}$ (Figure 1b). Formation of the derivatives is evidenced by the dramatic decrease in the size of the empty-cage peaks and the appearance of large peaks just after the dead-time. The large peaks observed between 7 and 12 min in the HPLC trace of the reaction mixture (Figure 1b) were assigned to unreacted 9-methylantracene and 9-me-

thylantracene/fullerene adducts, supported by mass spectrometric data, which show that the 8 min peak is 9-methylantracene and that the 9 and 12 min peaks are derivatives of mixed fullerenes, each showing peaks for derivatized C_{60} , C_{70} , and C_{84} (Supporting Information). The shorter retention times are due to an increased solubility of the 9-methylanthrlyl derivatives in toluene.

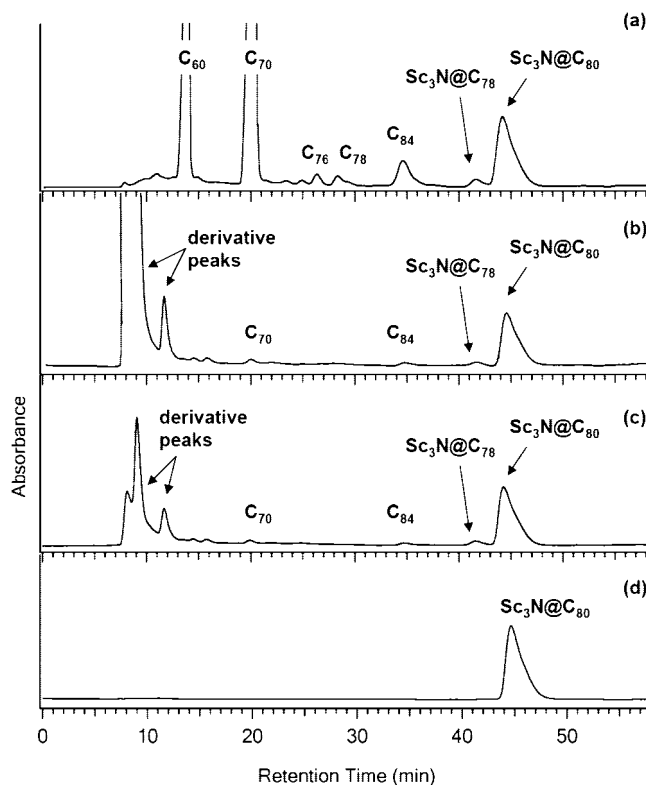


Figure 1. HPLC chromatograms of (a) extract of scandium soot, (b) extract of scandium soot after being heated with 9-methylantracene, (c) extract of scandium soot after being heated with 9-methylantracene and washed with ether, and (d) final purification by HPLC. HPLC conditions: 10 mm \times 250 mm PYE column at 2.0 mL min^{-1} flow rate with toluene, 390 nm detection.

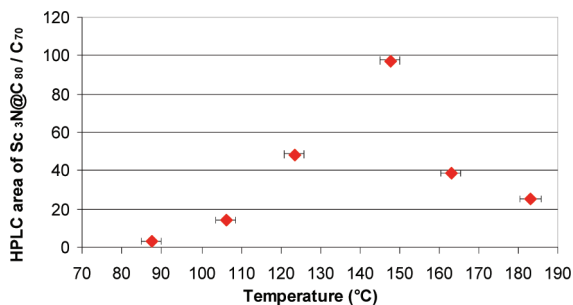


Figure 2. Enrichment of Sc₃N@C₈₀ vs C₇₀ as a function of reaction temperature (10:1 mass ratio of 9-methylanthracene to soot extract).

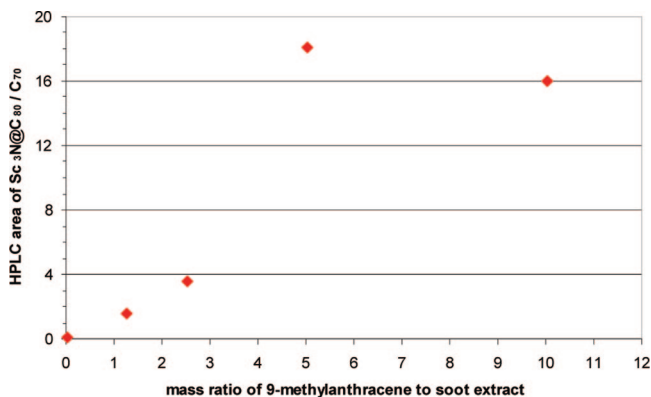


Figure 3. Enrichment of Sc₃N@C₈₀ vs C₇₀ as a function of mass ratio of 9-methylanthracene to Sc soot extract (85–90 °C).

As seen in comparing Figure 1a,b, the derivatization of the empty-cage fullerenes is very dramatic. From the areas calculated by integration, the Sc₃N@C₈₀ peak in the soot extract (Figure 1a) was 0.3 times the size of the C₇₀ peak, but after reaction with 9-methylanthracene (Figure 1b), the Sc₃N@C₈₀ peak was 42 times the size of the C₇₀ peak, a 140-fold increase in the ratio of Sc₃N@C₈₀/C₇₀. To perform the solid–liquid extraction, the reaction mixture was pulverized, sonicated in ether, and centrifuged, and subsequently, the supernatant was removed with a pipet. This method afforded Sc₃N@C₈₀ that was ~35% pure (Figure 1c) and Lu₃N@C₈₀ (Figure 4c) that was ~19% pure: 2.5- and 3.5-fold increases in purity, respectively. Considering the large differences in the retention times of adducts and the TNT EMFs on the HPLC column, a short HPLC column can be used, significantly reducing the time for final cleanup. After extensive washing, removal of the ether-soluble derivatives was accompanied by the loss of a small quantity of TNT EMF, either due to solid particles that did not settle out or due to particles that were disturbed in the removal of the liquid.

To further characterize the derivatization process, the ratio of empty-cage fullerenes to Sc₃N@C₈₀ was examined as a function of temperature for a reaction time of 30 min. It was determined that increasing the temperature to ~145 °C increased the reaction of empty-cages, while increasing the temperature above 145 °C facilitated the retro-reaction (Figure 2). Predictably, we also found that increasing the mass ratio of 9-methylanthracene to soot increased the yield of derivatives, but only up to a point after which little increase seemed to occur. The mass ratio for maximum yield of empty-cage derivatives from scandium soot extract was

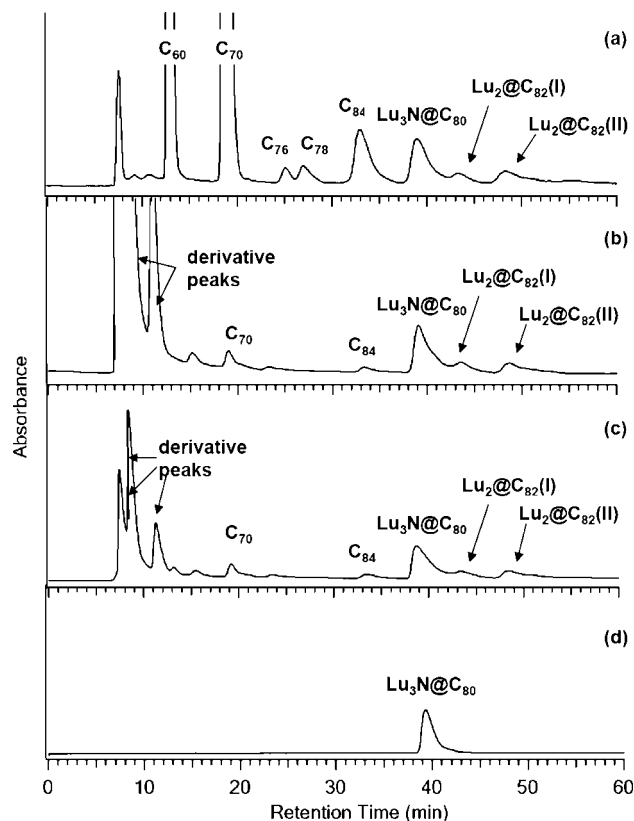


Figure 4. HPLC chromatograms of (a) extract of lutetium soot, (b) extract of lutetium soot after heating with 9-methylanthracene, (c) extract of lutetium soot after heating with 9-methylanthracene and washing with ether, and (d) final purification by HPLC. HPLC conditions: 10 mm × 250 mm PYE column at 2.0 mL min^{−1} flow rate with toluene, 390 nm detection.

found to be 5:1 (Figure 3). This corresponds to a 19-fold molar excess of 9-methylanthracene if it is assumed that all of the soot is C₆₀; since this is the smallest fullerene present, the actual molar excess is higher.

To determine the extent of reaction, the ratio of the HPLC peak area of Sc₃N@C₈₀/C₇₀ was calculated. We used the C₇₀ peak as a reference because it was better resolved. Also, C₇₀ seemed to undergo the retro-reaction most easily of all of the derivatives and therefore was the most sensitive for determining optimal conditions.

To test the applicability of this method for other C₈₀ cage TNT EMFs, a reaction using Lu-based soot was run under the optimal conditions determined for the Sc soot extract (i.e., 30 min at 145 °C, with a 5:1 mass ratio) (Figure 4). For these conditions, the empty-cage derivatives had almost completely reacted (Figure 4b). In the soot extract (Figure 4a), the ratio of Lu₃N@C₈₀ to C₇₀ was 0.11, but after reaction with 9-methylanthracene (Figure 4b), the ratio was 5.6, a 51-fold increase in the ratio of Lu₃N@C₈₀ to C₇₀. It is worth noting that two isomers of dimetallofullerenes Lu₂@C₈₂, Lu₂@C₈₂ (I) and Lu₂@C₈₂ (II), remain unreacted after heating with 9-methylanthracene (see Supporting Information), perhaps due to the low reactivity of Lu₂@C₈₂ or the rapid retro-reaction of its 9-methylanthracene adducts.

Clearly, alternative methods could be used to separate 9-methylanthracene derivatives of empty-cage fullerenes from the unreacted TNT EMF molecules more effectively. Komatsu and co-workers were able to separate C₆₀ from

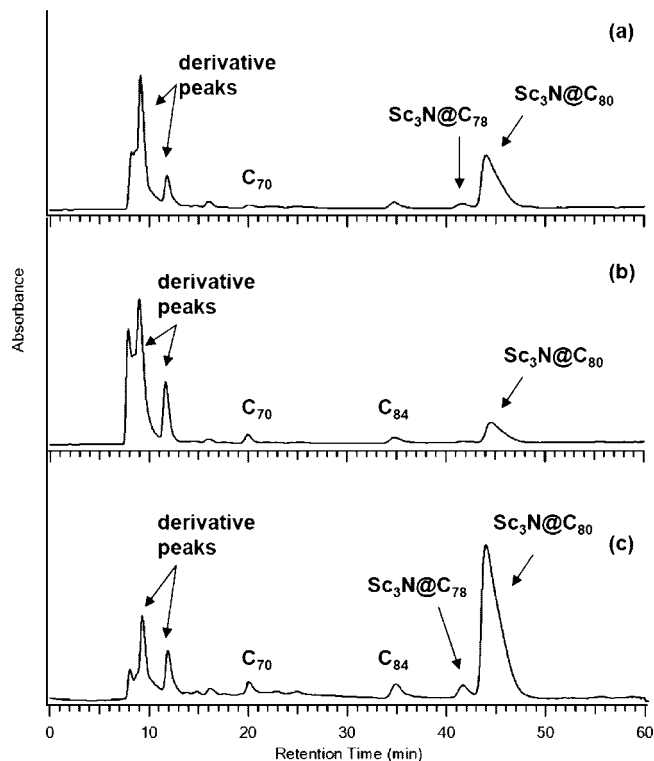


Figure 5. HPLC chromatograms of (a) solid extract of scandium soot after heating with 9-methylanthracene and washing with ether, (b) first fraction from the silica column with ethyl/toluene (v/v 3:7) as eluent, and (c) second fraction from the silica column with toluene as eluent. HPLC conditions: 10 mm \times 250 mm PYE column at 2.0 mL min⁻¹ flow rate with toluene, 390 nm detection.

9-hydroxymethylanthracene/ C_{60} derivatives on a silica column with toluene as the eluent.³⁴ Although we were not able to completely separate empty-cage 9-methylanthracene derivatives and TNT EMFs on a silica gel column, the enrichment purity was improved substantially. For example, the solid Sc soot extract after heating with 9-methylanthracene and washing thoroughly with ether (Figure 5a) was applied to a silica column. The column was initially flushed with ethyl ether/toluene (3:7 v:v). As shown in Figure 5b, the first fraction consisted of mainly derivatives along with 10% $Sc_3N@C_{80}$. The second fraction was collected when the column was subsequently flushed with toluene. From the

HPLC trace of the second fraction (Figure 5c), the percentage of $Sc_3N@C_{80}$ in the mixture increased to $\sim 60\%$. This represents a significant improvement since HPLC was not employed and the total workup time (including the Soxhlet extraction) was <24 h.

Conclusion

We developed a support-free chemical method to separate TNT EMFs from empty-cage fullerenes produced in a Krätschmer–Huffman generator. Our purification process exploits (i) the lower reactivity of TNT EMFs toward 9-methylanthracene via a Diels–Alder cycloaddition reaction and (ii) the solubility differences of unreacted TNT EMFs versus 9-methylanthracene-derivatized empty-cage fullerenes (C_{60} , C_{70} , etc.). For example, heating 9-methylanthracene with the Sc- or Lu-based soot extract yields 9-methylanthracene-derivatized empty-cage fullerenes that were subsequently removed by being washed with diethyl ether. The washed extract was then applied to a silica gel column and subsequently flushed with toluene. For the case of $Sc_3N@C_{80}$, the purified mixture increased to $\sim 60\%$ in a time period of <24 h. This represents a significant improvement in the purification process since HPLC was not employed to this point in the workup process. High-purity ($>99\%$) samples of the TNT EMFs can then be achieved by a final single-stage HPLC step with a minimum of solvent. This support-free chemical separation method has the advantages of being inexpensive, easily scalable, and faster than current purification methods.

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Supporting Information Available: Figures S1–S4 (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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