Nonchromatographic "Stir and Filter Approach" (SAFA) for Isolating $Sc_3N@C_{80}$ Metallofullerenes

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Abstract: Separation difficulties have led to a paucity of purified metallic nitride fullerenes (MNFs). Fundamental research and application development has been hampered with limited sample availability. Separation techniques designed to remove contaminant empty-cage fullerenes (e.g., C_{60}, $C_{70}...C_{2n}$) and classical metallofullerenes (e.g., non-MNFs) traditionally require expensive and tedious chromatographic methods. Our motivation is an alternative purification approach to minimize dependence on HPLC. Herein we report the use of cyclopentadienyl (CPD) and amino functionalized silica to selectively bind contaminant fullerenes. This "Stir and Filter Approach" (SAFA) provides purified MNF samples at ambient and reflux conditions. Under reflux conditions, purified MNFs (80% recovery, 41 h) are obtained using CPD silica. However, at room temperature, there is an equilibrium established between fullerenes and CPD silica, and no purified MNF samples are obtained using SAFA. In contrast, purified MNF samples (99+%) are readily obtained at room temperature using amino, diamino, and triamino silica at recoveries of 93% (11 h), 76% (9 h), and 50% (6 h), respectively.

Introduction

Metallic nitride fullerenes[1] (MNFs) offer multidisciplinary opportunities to investigate their fundamental properties and develop applications. Synthesized using the electric-arc process,[2] MNFs consist structurally of a trigonal planar[1] or slightly pyramidalized[3] cluster of atoms encapsulated within a fullerene. The carbon cage housing receives significant charge transfer from the entrapped metals.[4–8] Judicious selection of metals affords a rich array of unique properties to the scientific community.

A major hurdle to research is a limited availability of purified samples. Traditional HPLC methods[1] for MNFs are unfavorable due to expense (e.g., equipment, solvent waste, and columns), poor throughput (e.g., low solubility of MNFs in typical mobile phases), and the presence of fullerene contaminants coextracted from electric-arc soot. C_{60} and C_{70} fullerenes dominate the soluble product distribution with minor amounts of higher cage

fullerenes such as C_{78}, C_{82}, C_{84}, C_{86}, C_{88}, $C_{90}....C_{2n}$ ($n > 39$) and classical metallofullerenes ($A_m@C_{2n}$, A = metal, $m = 1–4$) that also must be removed. Recent MNF separation schemes include the use of cyclopentadiene (CPD) immobilized on a Merrifield resin[9] as a reactive support for fullerene uptake in a flash chromatographic column.[10] This approach represents a reactive extraction of fullerene contaminants. A selective electrochemical method has also been described as an alternative approach for isolating classical metallofullerenes[11] and MNFs.[12]

With the Merrifield resin approach, purified $Sc_3N@C_{80}$ MNF was isolated from extract in 2 days. [10] This method represents a significant improvement over HPLC. Although the CPD-resin approach is expensive and requires flow, it is possible to recover CPD-bound fullerenes. Motivations for our approach include a desire to (1) place the CPD moiety on a less expensive solid support, e.g., silica gel; (2) explore the separation efficiency of non-CPD reactive functional groups (e.g., amino) that also would exhibit selective fullerene uptake; and (3) develop an approach that is nonchromatographic and would require no flowing solvents. This new experimental design can be described as a "stir and filter approach" (SAFA), whereby the fullerene extract is added to a slurry of reactive silica gel, stirred, and filtered. The unreactive MNFs would be the only fullerenes in the filtrate.

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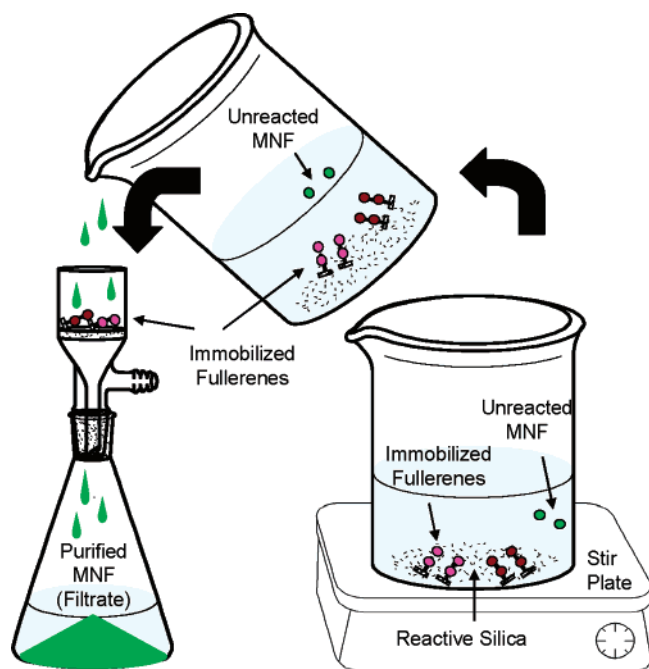(8) Campanera, J. M.; Heggie, M. I.; Taylor, R. *J. Phys. Chem. B* **2005**, *109*, 4024–4031.

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Figure 1. Schematic of the "Stir and Filter Approach" (SAFA) to purifying MNF samples.

Table 1. Comparison of Bond Resonance Energies of Fullerene Cages (from Refs 4, 10, 37)

fullerene species	carbon cage symmetry	bond resonance energy/β	predicted reactivity rank
C_{60}	I_h	+0.0822	5
C_{70}	D_{5h}	+0.0519	3
C_{76}	D_2	+0.0074	1
C_{78}	D_3	−0.0098	2
C_{84}	D_{2-1}	+0.0819	4
C_{68}^{6-} (MNF)	D_3	+0.155	6
C_{78}^{6-} (MNF)	D_{3h}	+0.1620	7
C_{80}^{6-} (MNF)	I_h	+0.1931	8

We hypothesized that an optimal amine loading, an appropriate temperature, and sufficient reaction time would result in preferential binding of aminosilica to fullerene contaminants. A schematic describing SAFA is shown in Figure 1.

This "selective reactivity" hypothesis is supported by recent reports (1) that MNF structures have significant electron transfer from the entrapped cluster to the cage surface,[4−6,32,33] (2) that MNFs are closed shell species,[5,33] and (3) that MNF C_{80} cages are more chemically inert relative to other fullerenes.[4,10,34−36]

Table 1 provides a list of fullerene cages and their respective bond resonance energies (BRE), with a more positive value being the least reactive. From these theoretical predictions,[4,37] MNFs (e.g., $Sc_3N@C_{68}$, $Sc_3N@C_{78}$, and $Sc_3N@C_{80}$) would be more chemically inert than empty-cage fullerenes. These calculations are supported with experimental data from four functionalized silica gels.

Results and Discussion

A. Preparation of Functionalized Silica Gels. The use of aminosilanes[38−48] as a coupling agent to silica gel is well-known. We evaluated cyclopentadienyl (0.5 mmol/g), amino (1.6 mmol/g), diamino (1.2 mmol/g), and triamino (0.96 mmol/g) silica for use in MNF separations. As a control, we also prepared *n*-propyl silica (1.1 mmol/g).

In SAFA, fullerene contaminants would be immobilized on the solid support and trapped by the filter membrane.

To demonstrate SAFA, we report functionalized silica gels (amino, diamino, and triamino) which exhibit a reaction mechanism[13] (i.e., electron transfer and addition) different from the CPD mechanism (i.e., 4 + 2 cycloaddition).[14−19] The CPD approach is investigated primarily as a comparison to fullerene uptake with amino functionalized silica. Selection of amino functional groups is based on our difficulty aminating the MNF cage. In contrast, amino groups[19−31] react with ease with C_{60}.

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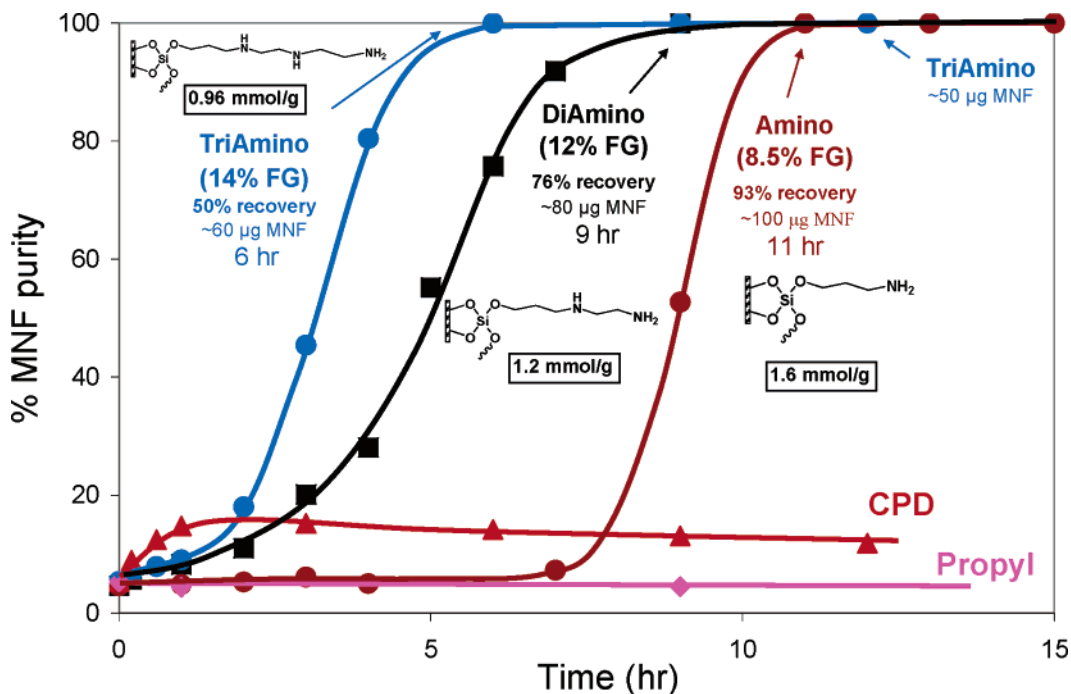
Figure 2. Percent MNF purity versus reaction time with functionalized silica at room temperature using SAFA.

B. Room-Temperature Isolation of MNFs from Soot Extracts with Functionalized Silica. Ambient conditions are important for fundamental, ease-of-use, and economical reasons. Raw extracts from electric-arc vaporization of Sc_2O_3/graphite rods produce complex mixtures of empty-cage fullerenes, classical metallofullerenes, and metallic nitride fullerenes.[1] The C_{60} and C_{70} fullerenes ($\sim$80−90%) typically dominate the extract distribution with $\sim$6% representing $Sc_3N@C_{80}$ MNFs.

As a control experiment to demonstrate the lack of MNF uptake by nonreactive silica, 1.5 mg of fullerene extract ($\sim$0.1 mmol fullerenes) in 15 mL of toluene were mixed with *n*-propyl silica (3 g, 3.3 mmol). The slurry was stirred under ambient temperature without N_2 for 1, 9, 22, 31, and 42 h. The percent MNF purity as a function of time is shown in Figure 2. HPLC analysis of the product mixture at 42 h indicated a 98% recovery of MNF. The 2% loss of MNF is likely due to adsorption to silica gel.

To investigate fullerene uptake with reactive silica gels, the same extract solution ($\sim$0.1 mmol fullerenes) was used for subsequent CPD, amino, diamino, and triamino experiments. When this fullerene solution ($\sim$0.1 mmol fullerenes) was mixed with CPD silica (3 g, 1.5 mmol) at room temperature, the MNF purity increased only slightly to 9.6%, despite 41 h of reaction time. With this molar excess of CPD functional group, the CPD silica−fullerene mixture reached an equilibrium state of bound and unbound fullerene with an MNF purity of only $\sim$10% (Figure 2).

To explore a different class of reactive silica at room temperature, SAFA experiments were designed with alkyl substituted, amino functional groups. Loadings of functional groups were determined by elemental analysis and thermal gravimetric analysis. Specifically, the average loadings of functional groups were amino (1.6 mmol/g), diamino (1.2 mmol/g), and triamino (0.96 mmol/g). When reacted with a $\sim$0.1 mmol fullerene solution described above, all three aminosilica gels used in SAFA permitted purified samples of MNFs in 99+% purity.

As shown in Figure 2, the trend with amino-based silica gels is a faster MNF purification time with increasing number of amino groups. The penalty for rapid purification time is a reduced recovery of MNF. The molar ratios used for these dilute fullerene solutions ($\sim$0.1 mmol fullerene) were 4.8 mmol amino, 3.6 mol diamino, and 2.9 mmol triamino functional groups. Mass determinations of purified samples were in the sub-milligram range, as expected, based on only 1.5 mg of fullerene extract at the beginning of the reaction.

C. Scalability Assessment using Amino-Based Silica at Room Temperature. A key issue in the research and development of MNFs is both purity and quantity. The SAFA experiments described in Figure 2 used very dilute solutions of fullerenes (0.1 mg/mL, $\sim$0.1 mmol) in 15 mL of toluene. Under those experimental parameters, MNF samples were isolated in high purity (99+%) but in low quantities (50 to 100 μg).

To assess scalability, 50 mg of fullerene extract (2.0 mg/mL, $\sim$2.5 mmol) were dissolved in 25 mL of *o*-xylene and mixed with either 10 g diaminosilica (12 mmol) or 10 g triaminosilica (9.6 mmol). From these 50 mg samples, purified MNFs (>99%) were obtained for these diamino and triamino silicas by stirring the fullerene mixture for 2 days. Isolated amounts of MNF samples were 2.5 to 3.5 mg (recoveries 76%-85%), depending on the type of reactive silica and length of reaction time.

As a representative example, the reaction of fullerene extract (50 mg, $\sim$2.5 mmol) with diamino silica (10 g, 12 mmol) was followed with time as shown in Figure 3. Results indicated a rapid uptake of higher mass empty-cage fullerenes and non-MNF metallofullerenes (e.g., $Sc_2@C_{82}$, $Sc_2@C_{84}$). Removal of empty-cage fullerenes occurred after 44 h. The reaction mixture was filtered, and solvent was removed from the filtrate. The isolated sample had a mass of 3.5 mg. HPLC analysis indicated the presence of MNFs at a purity of >99%. The composition of this 3.5 mg sample was 96% $Sc_3N@C_{80}$, with traces of $Sc_3N@C_{68}$ (3%) and $Sc_3N@C_{78}$ (1%) MNFs. A higher purity
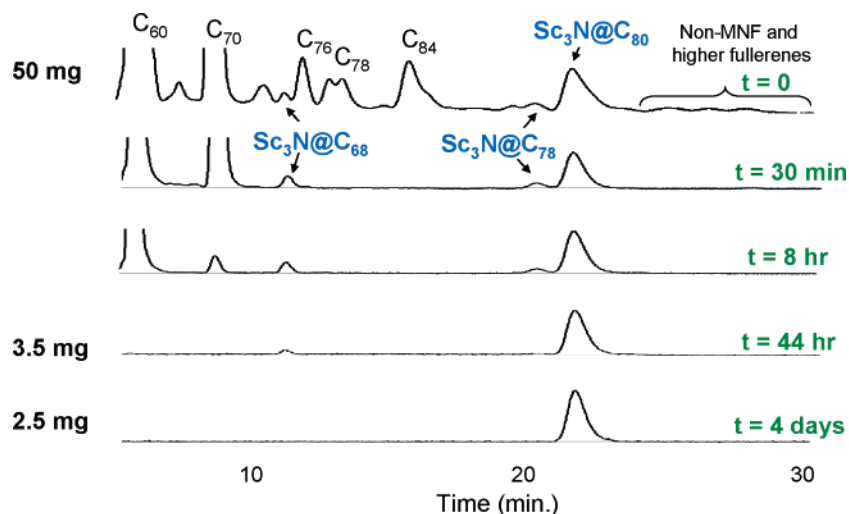
Figure 3. HPLC chromatograms for unreacted fullerene species in solution at various times for the reaction of diamino silica (12 mmol) with 50 mg of fullerene extract (∼2.5 mmol). Chromatographic conditions are 0.8 mL/min toluene, PYE column, 360 nm UV detection, and 50 μL injection.
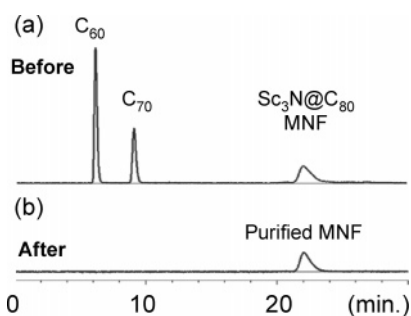

Figure 4. HPLC chromatograms demonstrating the feasibility of SAFA at reflux (a) an equimolar mixture of 12 μM (0.18 μmol each) C_{60}, C_{70}, and $Sc_3N@C_{80}$ before reaction with CPD silica (1.5 mmol) and (b) the filtrate after 41 h. Chromatographic conditions are 0.8 mL/min toluene, PYE column, 360 nm UV detection, and 50 μL injection.

sample of $Sc_3N@C_{80}$ (2.5 mg, >99%) was obtained by repeating the experiment with a longer reaction time (4 days).

D. Reflux Temperature Isolation of MNFs from Soot Extracts with Functionalized Silica. Extraction of fullerenes and MNFs from electric-arc soot is often performed under reflux conditions. Simulating these extraction conditions, we also investigated fullerene uptake at elevated temperatures. Note that purified MNF samples were obtained at room temperature using SAFA only with amino-based silica. Although SAFA with CPD silica at room temperature did not result in pure samples, the role of temperature in MNF separations had not yet been investigated for CPD (or the amino-based silicas).

To investigate the effect of temperature on selective fullerene uptake, 15 mL of an equimolar ternary mixture (0.18 μmol each) of C_{60}, C_{70}, and $Sc_3N@C_{80}$ was reacted with CPD silica (3.0 g, 1.5 mmol). In refluxing toluene (41 h), a selective uptake of C_{60} and C_{70} fullerenes onto CPD silica occurred as shown in Figure 4. The recovery of $Sc_3N@C_{80}$ MNF (99% purity) was 76% for this test mixture.

To assess the feasibility of SAFA at reflux for soot extracts, a fullerene extract solution (∼0.1 mmol fullerenes, 15 mL toluene) was stirred with CPD silica (1.5 mmol). Filtrates for reaction mixtures were analyzed by HPLC. Shown in Figure 5 are results of MNF purity using SAFA with CPD silica at reflux and room temperature. Results indicate purified MNFs (98%) at 80% recovery in 41 h. A MALDI-TOF mass spectrum for

isolated $Sc_3N@C_{80}$ using CPD with SAFA (reflux, 41 h) is shown in Figure 6b.

E. Uptake-Time Study of Fullerenes with CPD Silica at Elevated Temperature. To determine optimal reaction times for elevated temperatures (reflux), an experiment was designed to vary fullerene uptake with reaction time. In these experiments, 15 mL of fullerene extract (∼0.1 mmol) was reacted with 3.0 g of CPD silica (1.5 mmol). Aliquots were analyzed using HPLC. For clarity, only the molar concentrations of C_{60}, C_{70}, and $Sc_3N@C_{80}$ MNFs are shown as a function of time (Figure 6a). Mass spectral and HPLC data indicate higher fullerenes (e.g., C_{76}, C_{78}, C_{84}) and classical metallofullerenes (e.g., $Sc_2@C_{82}$, $Sc_2@C_{84}$) are readily removed with CPD silica. Results indicate factors of 10 and 4 for removal of C_{60} and C_{70}, respectively, in only 1 h. After 9 h, the concentrations of C_{60} and C_{70} are almost equal, and further reaction time (20 h) results in more unreacted C_{70} (1.3 μM) than C_{60} (0.8 μM).

This reactivity preference of C_{60} versus C_{70} for CPD silica is in contrast to amino-based silicas. The C_{60}/C_{70} selectivity differences between amino-based and CPD-based silica gels may be explained by differences in their binding mechanism. The amino−fullerene reaction[19,20,22,26−31] has been described as an electron-transfer/addition mechanism. The CPD−fullerene equilibrium[16−18,49] represents a Diels−Alder type cycloaddition reaction with a reversible covalent attachment process.

To evaluate MNF purity, aliquots of filtrates from 30 and 41 h were analyzed by mass spectrometry. The filtrate at 41 h had fewer $Sc_3N@C_{68}$ and $Sc_3N@C_{78}$ impurities. Shown in Figure 6b is the MALDI-TOF mass spectrum for the 41 h sample. The purity for isolated $Sc_3N@C_{80}$ was 98% (by HPLC), with only a trace of residual $Sc_3N@C_{78}$.

F. Effect of CPD Silica Loading on $Sc_3N@C_{68}$, $Sc_3N@C_{78}$, and $Sc_3N@C_{80}$ MNFs. An experiment to determine the effect of CPD silica loading (0.5 mmol/g) with Sc fullerene extract (0.1 mmol, 15 mL toluene) was also performed. Results are shown in Figure 7. In these experiments, a loading of 15 wt % of CPD silica (1.1 mmol) in refluxing toluene (41 h) resulted in a filtrate containing only MNF species, $Sc_3N@C_{68}$, $Sc_3N@C_{78}$, and $Sc_3N@C_{80}$ (Figure 7b). A slight increase to 20 wt % CPD

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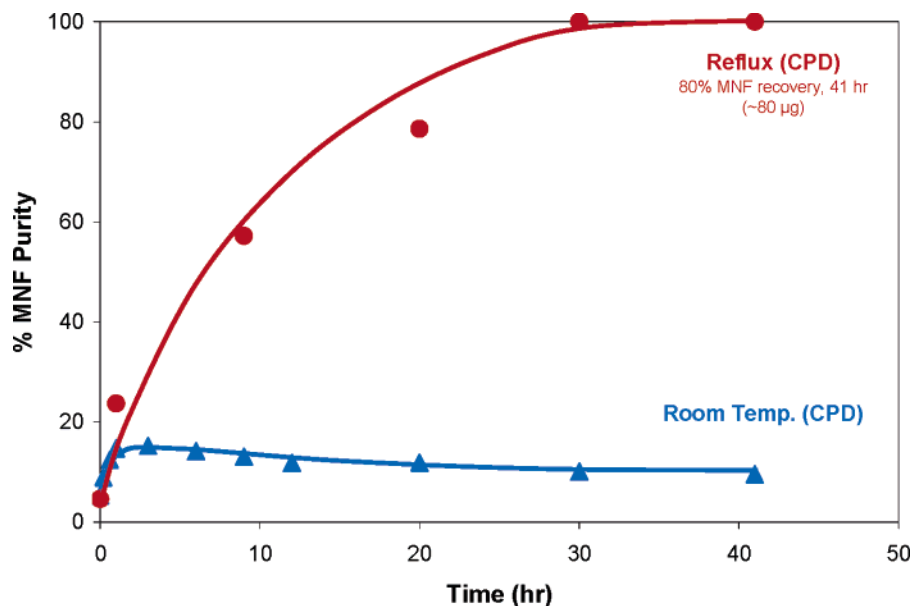
Figure 5. Effect of temperature on MNF purity: SAFA results from the reaction of CPD silica (1.5 mmol) and fullerene extract (~0.1 mmol).
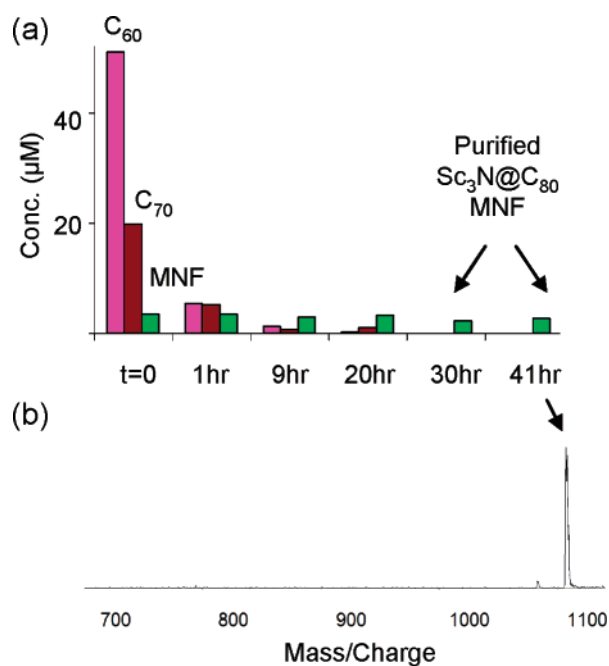

Figure 6. (a) Unreacted fullerene species in solution at various reaction times using CPD silica (0.5 mmol/g) and (b) MALDI-TOF mass spectrum of purified MNF material isolated from CPD silica (1.5 mmol) and Sc fullerene extract (~0.1 mmol fullerenes) in refluxing toluene (41 h).

silica (1.5 mmol), also at 41 h, removed $Sc_3N@C_{68}$ and further decreased $Sc_3N@C_{78}$ for an improved $Sc_3N@C_{80}$ sample (98% purity). Silica loading experiments with 3 wt % (0.19 mmol), 6 wt % (0.38 mmol), and 11 wt % (0.75 mmol) CPD silica were also performed. Results, however, for these lower loadings of CPD silica indicated residual empty-cage fullerene contaminants.

It should be noted that refluxing toluene experiments of extract stirred with amino-functionalized silica were also investigated using the SAFA technique. HPLC analysis of these reaction mixtures indicated longer reaction times.

Conclusions

We describe a "stir and filter approach" (SAFA) for isolating MNF samples. Purified $Sc_3N@C_{80}$ MNF (98+%) is readily
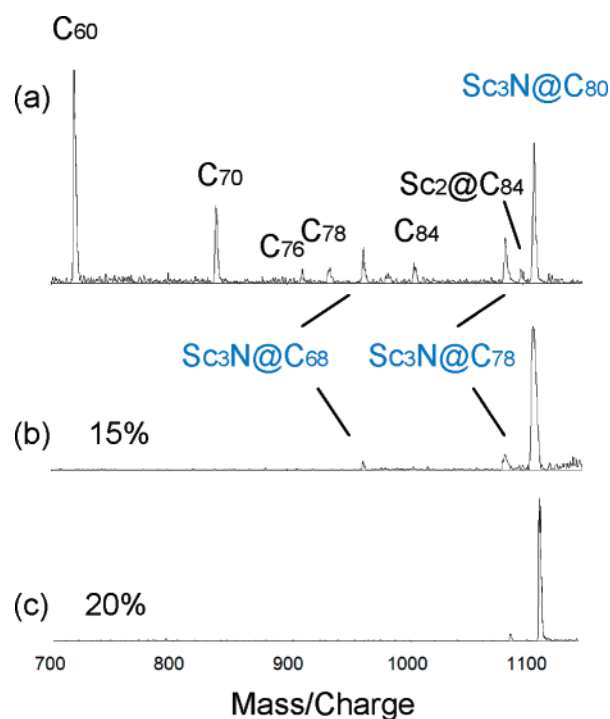

Figure 7. Effect of CPD loading amount on MNF species: MALDI-TOF mass spectra, positive ion mode, (a) soot extract from reactor, (b) CPD silica, 1.1 mmol, 15% (w/w), and (c) CPD silica, 1.5 mmol, 20% (w/w).

obtained at room temperature using triamino silica (0.96 mmol/g, 6 h, 50% recovery), diamino silica (1.2 mmol/g, 9 h, 76% recovery), or amino silica (1.6 mmol/g, 11 h, 93% recovery). The reactivity trend at room temperature (dilute fullerene solutions, toluene) with alkyl-substituted amines is triamino > diamino > amino silica. CPD silica experiments at room temperature using SAFA were unsuccessful in purifying MNFs. Under elevated temperatures, however, MNFs (98%) were successfully isolated using SAFA with CPD silica (41 h, 80% recovery). Scalability tests were performed for SAFA experiments using amino-based silica. Milligram quantities (3 mg) of purified $Sc_3N@C_{80}$ were isolated after 2 days of stirring 50 mg

Table 2. Summary of Silica Gel Characterization by Elemental Analysis (EA) and Thermal Gravimetric Analysis (TGA)

	Weight % Carbon (EA)	Weight % Functional Group, FG (TGA)	Loading (mg FG/g)	Loading (mmol FG/g)	Surface Coverage (μmol FG/m^2)
Cyclopentadienyl Silica Gel 2	3.9% C	6.3% FG	EA: 43, TGA: 63 **Avg. 53**	EA: 0.41 TGA: 0.59 **Avg. 0.50**	EA: 0.81 TGA: 1.2 **Avg. 1.0**
MonoAmino Silica Gel 3	6.0% C	8.5 % FG	EA: 96 TGA: 85 **Avg. 91**	EA: 1.7 TGA: 1.5 **Avg. 1.6**	EA: 3.3 TGA: 2.9 **Avg. 3.1**
DiAmino Silica Gel 4	7.1% C	12 % FG	EA: 120 TGA: 120 **Avg. 120**	EA: 1.2 TGA: 1.1 **Avg. 1.2**	EA: 2.4 TGA: 2.3 **Avg. 1.9**
TriAmino Silica Gel 5	8.2% C	14 % FG	EA: 140 TGA: 140 **Avg. 140**	EA: 0.97 TGA: 0.94 **Avg. 0.96**	EA: 1.9 TGA: 1.9 **Avg. 1.9**

of fullerene extract with amino-based silicas at room temperature. This feat is noteworthy as the entire purification method (SAFA) was done without HPLC.

Experiments using SAFA to isolate other MNFs (e.g., $Gd_3N@C_{80}$, $Lu_3N@C_{80}$, $Er_3N@C_{80}$, etc.) and other reactive silicas are being investigated. Advantages of SAFA over current MNF separations are as follows: (1) no chromatography equipment, (2) no flowing solvent, (3) rapid separation time (4) no electrochemical equipment, (5) room temperature separations, (6) aerobic conditions, (7) inexpensive chemicals to make functionalized silica, (8) unattended separation, and a (9) scalable process for industry. Also of significance is the ability to "tune" the selection of MNF distribution as a function of silica loading. One can obtain a sample containing all three MNF cages of 68, 78, and 80 atoms or simply increase the amount of reactive silica and/or reaction time to obtain the $Sc_3N@C_{80}$ species.

Experimental Section

Materials and Methods. Graphite rods ($^1/_4$" × 6", 99.99+%) were purchased from Alfa Aesar and used as received. Graphite powder (99.5%, 325 mesh) and Sc_2O_3 (99.9%, 325 mesh) were purchased from Cerac. Graphite rods were core-drilled and packed with 3 mol % of Sc_2O_3. Graphite and metal oxide powders were mixed in a mortar and pestle prior to packing. Packed rods were placed in a tube furnace (1080 °C) for 12 h under nitrogen, cooled, placed in the electric-arc reactor, and vaporized. Soot was extracted with *o*-xylene (98%, Aldrich). From one $^1/_4$" packed rod, 3.1 g of soot were produced. For the dried extract (52 mg), the amount of MNF available for isolation would be ~3 mg. The MNF abundance in the extract is ~6%. The MNF percentage in the raw soot is ~0.1%. C_{60} and C_{70} fullerenes were purchased from MER and used as received to prepare 12 μM standard solutions in toluene. For HPLC separations, a 4.6 mm × 250 mm (PYE) pyrenyl-based column (SES Research) was used. Unfunctionalized silica gel was purchased from Aldrich with the following specifications: BET surface area of approximately 500 m^2/g, pore volume 0.75 cm^3/g, 70−270 mesh, and 60 Å (for column chromatography). Silanes were purchased from Gelest and used directly upon opening.

Electric-Arc Synthesis of Scandium Fullerene Soot Extracts. The electric arc production of fullerene and MNF soot is previously described.[1] The procedure involves a fixed graphite rod (anode) and a core-drilled consumable graphite rod (cathode) that is packed with metal oxide and vaporized in an electric arc reactor by resistive heating. For

$^1/_4$" rods, a current of 65 A is used with a gap voltage of 31 V. The consumable rod involves a $^1/_4$" × 6" cored graphite rod which is packed with Sc_2O_3 at 3 mol % with graphite to produce soot extract containing fullerenes, classical metallofullerenes, and MNFs. The source of nitrogen is N_2 (25 mL/min) in He buffer gas (625 mL/min).

Synthesis of *n*-Propyl-Functionalized Silica Gel. Toluene (~4000 mL) in a 5-L round-bottom flask with 250 g of silica gel was distilled under nitrogen to remove water azeotropically. When ~500 mL of distillate were collected, 75 g of *n*-propyltrimethoxysilane (Gelest) were added over a 20 min period. The reaction was stopped after 6 h. The solid product was rinsed with toluene, chloroform, methanol, chloroform, and hexane and vacuum-dried at 60 °C for 1 day (260 g) and stored in a desiccator. Elemental analysis indicated 3.80% C and 1.15% H. Using carbon data, an estimate of 1.1 mmol/g (45 mg/g) was calculated using the C_3H_7 (43 g/mol) moiety as the functional group (Table 2). A surface coverage of 2.1 μmol/m^2 was estimated based on 500 m^2/g of surface coverage for unfunctionalized silica (Aldrich).

Synthesis of Cyclopentadienyl-Functionalized Silica Gel. Toluene (~1500 mL) in a 2-L round-bottom flask with 100 g of silica gel was distilled under nitrogen to remove water azeotropically. When ~200 mL of distillate were collected, 25 g of 3-cyclopentadienylpropyltriethoxysilane were added over a 20 min period. The reaction was stopped after 6 h. The solid product was rinsed with toluene, chloroform, methanol, chloroform, and hexane. The silica gel product was vacuumdried (107.82 g) at 60 °C for 3 days and stored in a desiccator. Elemental analysis indicated 3.87%C, 1.12%H, and 0.0%N. Using carbon data, an estimate of 0.41 mmol/g (43 mg/g) was calculated using the C_8H_{11} (107 g/mol) moiety as the functional group (Table 2). A surface coverage of 0.81 μmol/m^2 was estimated based on 500 m^2/g of surface coverage for unfunctionalized silica (Aldrich).

Synthesis of Amino-Functionalized Silica Gel. Toluene (~2 L) in a 5-L round-bottom flask with 250 g of silica gel was distilled under nitrogen to remove water azeotropically. When ~500 mL of distillate were collected, 75 g of 3-aminopropyltriethoxysilane (Gelest) were added over a 20 min period. The reaction was stopped after 6 h. The solid product was rinsed with toluene, chloroform, methanol, chloroform, and hexane and vacuum-dried (277 g) at 60 °C for 1 day and stored in a desiccator. Elemental analysis indicated 5.97%C, 1.51%H, and 1.86%N. Using carbon data, an estimate of 1.7 mmol/g (96 mg/g) was calculated using the C_3H_8N (58 g/mol) moiety as the functional group (Table 2). A surface coverage of 3.3 μmol/m^2 is estimated based on 500 m^2/g of surface coverage for unfunctionalized silica (Aldrich).

Synthesis of Diamino-Functionalized Silica Gel. Toluene (~2 L) in a 5-L round-bottom flask with 250 g of silica gel was distilled under

nitrogen to remove water azeotropically. When ~500 mL of distillate were collected, 75 g of *N*-(2-aminoethyl)-3-aminopropyltriethoxysilane (Gelest) were added over a 20 min period. The reaction was stopped after 6 h. The solid product was rinsed with toluene, chloroform, methanol, chloroform, and hexane. The silica gel product was vacuum-dried (286 g) at 60 °C for 1 day and stored in a desiccator. Elemental analysis indicated 7.12%C, 1.89%H, and 2.97%N. Using carbon data, an estimate of 1.2 mmol/g (120 mg/g) was calculated using the $C_5H_{13}N_2$ (101 g/mol) moiety as the functional group (Table 2). A surface coverage of 2.4 μmol/m^2 was estimated based on 500 m^2/g of surface coverage for unfunctionalized silica (Aldrich).

Synthesis of Triamino-Functionalized Silica Gel. Toluene (~4000 mL) in a 5-L round-bottom flask with 250 g of silica gel was distilled under nitrogen to remove water azeotropically. When ~500 mL of distillate were collected, 70 g of (3-trimethoxysilylpropyl)-diethylene triamine (Gelest) were added over a 20 min period. The reaction was stopped after 6 h. The solid product was rinsed with toluene, chloroform, methanol, chloroform, and hexane. The silica gel product was vacuum-dried at 60 °C for 1 day (282 g) and stored in a desiccator. Elemental analysis indicated 8.16% C, 1.92% H, and 3.47% N. Using carbon data, an estimate of 0.97 mmol/g (140 mg/g) was calculated using the $C_7H_{18}N_3$ (144 g/mol) moiety as the functional group (Table 2). A surface coverage of 1.9 μmol/m^2 was estimated based on 500 m^2/g of surface coverage for unfunctionalized silica (Aldrich).

Thermogravimetric Analyses of Silica Gels. Thermal gravimetric analysis, TGA (TA Instruments 2050, 10 °C/min, air), of functionalized silica gels showed initial weight loss from 25 to 250 °C of 1.9, 2.1, 2.0, and 5.5 wt % for monoamino, diamino, triamino, and CPD silica, respectively. Initial weight loss was due to removal of adsorbed water and condensation of residual silanols. A second decrease in mass for each silica gel was observed at temperature ranges of ca. 250–800 °C, which can be attributed to the loss of functional groups. These loss values for monoamino, diamino, triamino, and CPD silica are 8.5, 12, 14, and 6.3 wt %, respectively. Loadings of functional group were calculated based on these weight losses and correspond to 1.5 mmol/g, 1.1 mmol/g, 0.94 mmol/g, and 0.59 mmol/g, respectively, for amino, diamino, triamino, and CPD silica. These estimates from TGA were comparable to loadings calculated from elemental analysis (Table 2).

Separation and Purification of Sc$_3$N@C$_{80}$ MNF from a Mixture of C$_{60}$ and C$_{70}$ Using CPD Silica. A standard solution of C$_{60}$, C$_{70}$, and Sc$_3$N@C$_{80}$ (0.18 μmol each) in 15 mL of toluene was prepared at 12 μM each. Two round-bottom flasks, each loaded with 2.22 g (1.1 mmol) and 2.96 g (1.5 mmol) of cyclopentadienyl silica, were mixed with 15 mL of this standard solution. Placed in 50 mL round-bottom flasks (14/20) with a vertical condenser, under a nitrogen atmosphere, the fullerene/silica gel mixtures were stirred under reflux for 41 h. Upon filtering with a PTFE membrane filter (0.50 μm), the filtrate was collected with the corresponding HPLC chromatogram as shown in Figure 4b.

Separation and Purification of Sc$_3$N@C$_{80}$ MNF from Soot Extract Mixtures Using Amino, Diamino, Triamino, and CPD Silica. Scandium fullerene soot from the electric-arc reactor was extracted with *o*-xylene and dried under rotary evaporation. A fullerene extract solution was prepared at 0.1 mg/mL toluene. For room-temperature experiments, a 50 mL round-bottom flask was charged with 15 mL of this stock solution (~0.1 mmol fullerenes) and 3.0 g amino silica (4.8 mmol), or 3.0 g diamino silica (3.6 mmol), or 3.0 g triamino silica (1.9 mmol), or 3.0 g CPD silica (1.5 mmol). This slurry was stirred for arbitrary reaction times. Aliquots of the reaction mixture were filtered through a PTFE membrane filter (0.50 μm) and injected into the PYE HPLC column for quantitative analysis. Chromatographic conditions were 0.8 mL/min toluene, 360 nm UV detection, and 50 μL injection. Reflux experiments were done in the same manner, with the following adjustments: a vertical condenser was placed atop the 50 mL flask, a nitrogen atmosphere was used, and a thermocouple/oil bath was used to heat the reaction mixture.

Scalability Study Using Amino-Based Silica Gel at Room Temperature. To a 125 mL round-bottom flask was added 50 mg of extract in 25 mL of *o*-xylene for a concentration of 2.0 mg/mL. To this extract solution (~2.5 mmol fullerenes) was added 10 g of diamino silica (12 mmol). The solution was stirred at room temperature, and aliquots were removed for HPLC analysis as described above. The experiment was repeated with 10 g of triamino silica (9.6 mmol).

Uptake and Time Study of Fullerenes with CPD Silica at Elevated Temperature. Extract solution (15 mL, ~0.1 mmol fullerenes) was placed in each of five 50 mL round-bottom flasks (14/20). To each flask was added 3.04 g of CPD silica (1.5 mmol). The flasks were heated at reflux, while stirring in a nitrogen atmosphere. Reactions were stopped at arbitrary time intervals of 1, 9, 20, 30, and 41 h. Filtrations were performed using 0.50 μm membrane filters, and filtrates were subsequently characterized by HPLC and MALDI-TOF mass spectrometry (Figure 6).

Effect of CPD Silica Loading on Sc$_3$N@C$_{68}$, Sc$_3$N@C$_{78}$, and Sc$_3$N@C$_{80}$ MNFs. Extract solution (15 mL, ~0.1 mmol fullerenes) was placed in each of five 50 mL round-bottom flasks (14/20). To each flask was added a stir bar and an arbitrary quantity of CPD silica, 0.38 g (0.19 mmol), 0.76 g (0.38 mmol), 1.52 g (0.76 mmol), 2.28 g (1.14 mmol), and 3.04 g (1.5 mmol) of CPD silica. Samples were stirred in refluxing toluene under nitrogen for 41 h, cooled, and filtered through a 0.50 μm membrane filter. The filtrate was then analyzed by HPLC and MALDI-TOF mass spectrometry (Figure 7).

Supporting Information Available: Complete references and TGA profiles for functionalized silica. This material is available free of charge via the Internet at http://pubs.acs.org.

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