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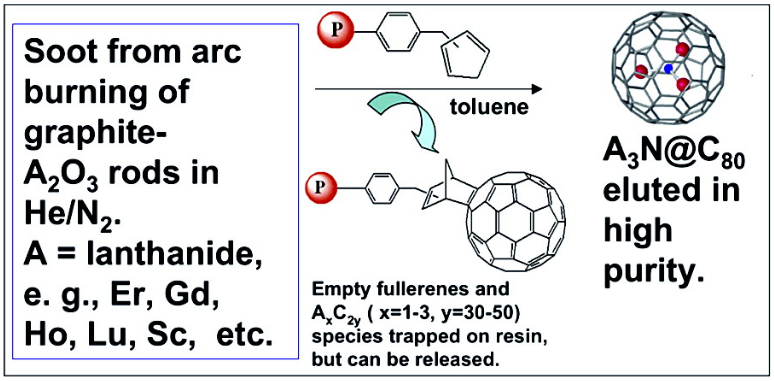
J. Am. Chem. Soc., **2005**, 127 (46), 16292-16298• DOI: 10.1021/ja055089t • Publication Date (Web): 28 October 2005



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Purification of Endohedral Trimetallic Nitride Fullerenes in a Single, Facile Step

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Abstract: A major hurdle hampering the development of fullerenes, endohedral metallofullerenes, and nanotubes has been the difficulty of obtaining high purity samples. Soots prepared in the usual manner via a Krätschmer-Huffman electric-arc generator consist of mixtures of insoluble carbonaceous materials and soluble fullerenes: C_{60}, C_{70}, C_{76}, C_{78}, C_{84}, etc. When metals are introduced as endohedral species the complexity of the resultant soot is even greater because of the presence of multiple isomers of both the empty fullerenes and the endohedral metallofullerenes. Here, for the first time, we report that lanthanide trimetallic nitride endohedral metallofullerenes, $A_3N@C_{80}$ (A = lanthanide atom, e.g., Er, Gd, Ho, Lu, Sc, Tb, Tm, Y), can be obtained in pure form directly from as-prepared soots in a single facile step by taking advantage of their extraordinary kinetic chemical stability with respect to the other fullerenes in Diels−Alder reactions with a cyclopentadiene-functionalized resin. We show that careful control of conditions (stoichiometry, time, temperature) allows separation of fullerenes with different cage sizes, as well as isomeric species. Furthermore, the Diels−Alder reaction is thermally reversible, and we demonstrated that the bound empty-cage fullerenes and classical endohedral metallofullerenes can be recovered by displacement with maleic anhydride.

Introduction

The scarcity of purified, homogeneous samples has hampered wider study and application of carbonaceous nanomaterials (fullerenes, endohedral metallofullerenes, and nanotubes). Production of single-walled nanotubes usually leads to distributions in terms of diameter, chirality, and length, and formation of multiwalled nanotubes.[1] The usual Krätschmer-Huffman (K−H) electric-arc generator produces a mixture of fullerenes including C_{60}, C_{70}, C_{76}, C_{78}, C_{84}, etc.[2] The complexity is even greater for endohedral metallofullerenes because of the presence of multiple isomers of both the fullerenes and metallofullerenes.[3] Until now, the only reliable methods for obtaining purified fullerene and endohedral metallofullerene (EMF) samples involved extensive, repetitive, time-consuming chromatographic procedures that required large volumes of solvent.

In this paper, we report that pure trimetallic nitride template (TNT) EMFs, $A_3N@C_{80}$ (A = lanthanide atom),[4−6] can be obtained from crude soots in a single, facile step based on selective chemical reactivity. These TNT EMFs are currently being seriously investigated for a number of diagnostic (MRI and X-ray contrast agents) and therapeutic medical applications.[7,8]

Our purification protocol is based on the kinetic stability of the TNT EMFs relative to empty-cage fullerenes and classical EMFs, such as $A_x@C_{2y}$ ($x = 1−3$, $y = 30−50$), which are concomitantly produced and also of interest in medical imaging.[8−10] Computational and experimental results demonstrate significant charge transfer (6 electrons) to the icosahedral (I_h symmetrical) cage of TNT EMFs, e.g., $[Sc_3N]^{+6}@[C_{80}]^{-6}$.[11,12]

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10.1021/ja055089t CCC: $30.25 © 2005 American Chemical Society

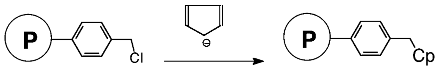
Table 1. Minimum Bond Resonance Energies of Reported Fullerenes (from ref 12)

species	symmetry	BRE/β	predicted reactivity rank[a]
C_{60}	I_h	+0.0822	26
C_{70}	D_{5h}	+0.0519	22
C_{76}	D_2	+0.0074	16
C_{78}	D_3	−0.0098	15
C_{78}	C_{2v-1}	−0.0440	9
C_{78}	C_{2v-2}	−0.0887	1
C_{82}	C_s	+0.0096	17
C_{82}	C_{s-2}	−0.0314	12
C_{82}	C_{2-1}	−0.0405	10
C_{82}	C_{2-2}	−0.0607	4
C_{84}	$D_{2-1}{}^{\dagger}$	+0.0819	25
C_{84}	$T_{\mathrm{d}}{}^{\dagger}$	+0.0771	24
C_{84}	D_{6h}	+0.0351	20
C_{84}	D_{2d}	+0.0108	18
C_{84}	D_{3d}	−0.0702	3
C_{84}	D_{2-2}	−0.0254	13
C_{84}	C_{s}	−0.0316	11
C_{84}	C_2	−0.0501	8
C_{84}	D_{2d-2}	−0.0564	6
C_{84}	D_{2-3}	−0.0574	5
$C_{68}{}^{-6}$	D_3	+0.155	28
$C_{78}{}^{-6}$	D_{3h}	+0.1620	29
$C_{80}{}^{-6}$	I_h	+0.1931	31
$C_{80}{}^{-6}$	D_{5h}	+0.1652	30
$C_{82}{}^{-4}$	$C_{s-1}{}^{b}$	+0.0743	23
$C_{82}{}^{-4}$	$C_{2-1}{}^{b}$	+0.0296	19
$C_{82}{}^{-4}$	$C_{2-2}{}^{b}$	−0.0212	14
$C_{82}{}^{-4}$	$C_{s-2}{}^{b}$	−0.0736	2
$C_{84}{}^{-4}$	D_{2d}	+0.0839	27
$C_{84}{}^{-4}$	C_s	+0.0430	21
$C_{84}{}^{-4}$	C_{2v-4}	−0.0514	7

[a] Highest reactivity = 1. [b] Not yet an isolated/identified isomer.

Aihara has calculated the minimum bond resonance energies (min BRE) for numerous fullerenes and metallofullerenes; negative BREs represent kinetic instability and higher chemically reactivity. This leads to the prediction of exceptional kinetic and thermodynamic stability of the icosahedral $[C_{80}]^{-6}$ cage of $A_3N@C_{80}$ that is significantly greater than neutral empty-cages C_{60} and C_{70}, which are the major products of the K−H process (Table 1).[12] Note that the min BRE value for the icosahedral $[C_{80}]^{-6}$ cage is the highest on the list, meaning it should be the least reactive in general. Consistent with this prediction, $Sc_3N@C_{80}$ is stable in air to temperatures of 600−650 K[13] and in nanotube "peapods" in vacuo to temperatures in excess of 1300 K.[14] An isochromanone derivative of $Sc_3N@C_{80}$ can be prepared only at elevated temperatures,[15] in comparison with the analogous lower temperature reaction with the empty-cage fullerene C_{60}.[16] Similarly, the Prato reaction of $Sc_3N@C_{80}$ produces a monoadduct[17] under conditions which yield multi-adducts with empty cage fullerenes[18a] and classical endohedral metallofullerenes.[18b] Recently, the low reactivity of $Sc_3N@C_{80}$ in comparison to $La_2@C_{80}$ (a singlet ground state in which the cage has been assigned[11,12] as the I_h hexaanion, $C_{80}{}^{-6}$) in photochemical disilarane cycloadditions has been reported and rationalized in terms of redox potentials.[19] Obviously, the nature of the endohedral species plays a role in the reactivity and even regiochemistry, as recently demonstrated for A = Y vs A = Sc of $A_3N@C_{80}$[20] and the recent production of a diadduct from reaction of $Gd_3N@C_{80}$ with the *o*-quinodimethane derived from 6,7-dimethoxyisochromanaone in less time (1 h @ 214 °C)[21] than for production of the monoadduct (predominantly) of the $Sc_3N@C_{80}$ analogue (24 h @ 214 °C).[15] Nonetheless, although not an absolute predictor of reactivities, the min BREs provide a useful framework for predicting and understanding the relative reactivities of fullerenes, EMFs and TNT EMFs.

Scheme 1. Synthesis of Cyclopentadiene (Cp)-Functionalized Resin **2**



1 **2**

Results and Discussion

A. Preparation of Reactive Resin for Purification of TNT EMFs and Other Fullerenes. On the basis of the observed low reactivity of the TNT EMFs, we reasoned that a suitably designed insoluble resin system could remove more reactive fullerenes from mixtures produced in the K−H process and allow the purification of the TNT EMFs in a facile manner. Fullerenes act as dienophiles in Diels−Alder cycloaddition reactions.[15,16,21−23] We, therefore, prepared a cyclopentadiene-functionalized styrene-divinylbenzene resin (**2**) from the chloromethylated (Merrifield) resin **1** in a fashion similar to the procedure reported by Rotello et al.[24] (Scheme 1). However, we used a lower level of cross-linking (1% vs 2%) and a higher loading of chloromethylated sites (3.5−4.5 vs 1.04 meq of Cl/g) for synthesis of resin **2**.

Figure 1 illustrates the concept; as the solution of the fullerene mixture passes through a column packed with the cyclopentadienyl resin **2** the species are bound to the resin by Diels-Alder cycloaddition in order of their reactivities, empty cages (green balls) first, then classical EMFs (pink balls) and under appropriate time/temperature conditions the TNT EMF (blue ball) is left unbound and can be isolated in a pure state in the eluent solution.

B. Purification of Synthetic Binary Mixtures of C_{60} with $A_3N@C_{80}$. As a first test of the concept, 1:1 (mass:mass, 1.5−2.0:1.0 mol:mol) binary mixtures of C_{60}, the predominant

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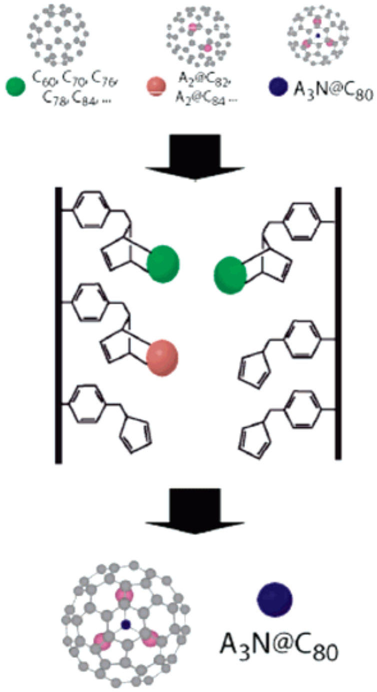

Figure 1. Separation of TNT EMFs from empty cage fullerenes and classical EMFs by selective cycloadditions with resin **2**.

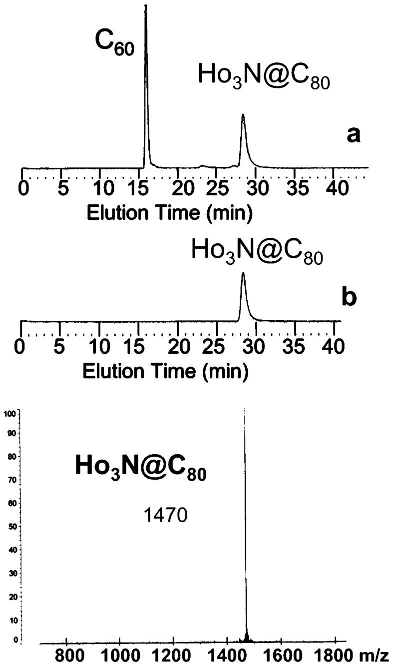

Figure 2. HPLC traces (Buckyclutcher column, toluene, 1 mL/min, detection at 390 nm) of (**a**) a synthetic mixture of C_{60} and $Ho_3N@C_{80}$ and (**b**) pure $Ho_3N@C_{80}$ obtained by application of the mixture to a column of resin **2** and flushing with toluene for 4 h at room temperature. (**c**) MALDI TOF mass spectrum (9-nitroanthracene matrix, negative ion) of the pure $Ho_3N@C_{80}$.

material formed in the K−H process in all cases, and the TNT EMFs were examined. Toluene solutions of the mixtures were applied to columns packed with resin **2** and toluene; the column was flushed with toluene and the resultant solution was analyzed by HPLC. The C_{60} was cleanly removed in every case, yielding pure lanthanide TNT EMFs, $Sc_3N@C_{80}$, $Gd_3N@C_{80}$, and $Ho_3N@C_{80}$. Figure 2 shows the results for purification of $Ho_3N@C_{80}$; see the Supporting Information for equivalently good results obtained for the other two mixtures.

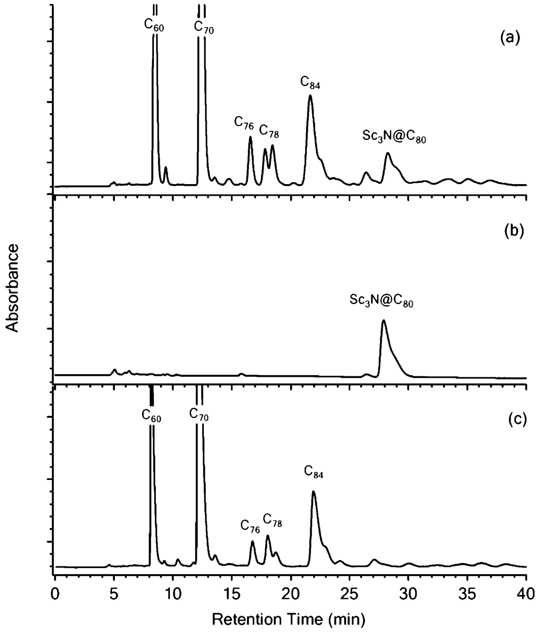

Figure 3. HPLC (PYE column, toluene, 3mL/min, detection at 390 nm) traces of (**a**) the toluene extract of "scandium soot", (**b**) the room-temperature toluene eluent from application of the extract to a column packed with cyclopentadiene-functionalized resin; the peak at 27.9 min corresponds to $Sc_3N@C_{80}$; there are minor peaks due to $Sc_3N@C_{68}$ (16 min) and $Sc_3N@C_{78}$ (27 min) and at retention times of 5−10 min due to unreactive polycyclic aromatic hydrocarbons from the soot; see further discussion below and (**c**) the eluent from the column after elution (b) upon heating at 85 °C in the presence of maleic anhydride.

C. Purification of $Sc_3N@C_{80}$ Soot Extract. Next we applied the purification protocol to the toluene extract of the soot produced from a K−H preparation of $Sc_3N@C_{80}$. The soot from the arc process with Sc_2O_3-loaded graphite rods was subjected to Soxhlet extraction with toluene. Figure 3a shows the HPLC trace of the toluene extract containing both empty cage fullerenes and $Sc_3N@C_{80}$. Figure 4 contains the CI mass spectrum of the extract, demonstrating the presence of empty cage fullerenes C_{60}, C_{70}, C_{76}, C_{78}, C_{82}, C_{84}, C_{86} (*m/z* 1032), C_{88} (*m/z* 1056), C_{90} (*m/z* 1080), C_{92} (*m/z* 1104), C_{94} (*m/z* 1128) and C_{96} (*m/z* 1152), along with TNT EMFs $Sc_3N@C_{68}$,[25] $Sc_3N@C_{78}$,[6] and $Sc_3N@C_{80}$.[4,5] The concentrated extract was applied to a column packed with resin **2** and the column was flushed slowly with toluene. As demonstrated above with the simple binary mixtures and in accord with Figure 1, the empty-cage fullerenes present in the extract react with the cyclopentadiene-functionalized resin by Diels−Alder cycloaddition, allowing the less reactive TNT EMF, $Sc_3N@C_{80}$ (see Table 1), to pass through (essentially completely unreacted as demonstrated below), thus affording relatively pure $Sc_3N@C_{80}$ (Figure 3b); see also the discussion of purification of the raw "scandium soot" below.

The Diels−Alder reaction is thermally reversible and Rotello et al. investigated recovery of C_{60} from similar cyclopentadiene-functionalized supports upon heating.[24,26] And Saunders et al. utilized the reversibility for isomer release after anthracene Diels−Alder adducts had been purified.[27]

Here, we demonstrated recovery of the empty-cage fullerenes trapped by resin **2**; Figure 3c shows the HPLC trace of the eluent

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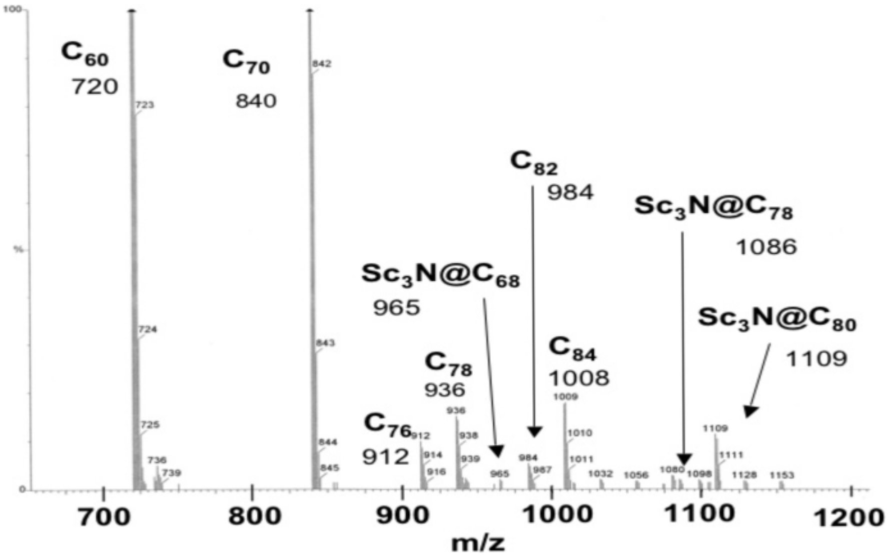

Figure 4. Chemical ionization mass spectrum (negative ion) of the toluene extract of soot made from graphite rods packed with Sc_2O_3; as indicated, empty cage fullerenes and TNT EMFs are present.

from the column upon heating at 85 °C in the presence of maleic anhydride. The overall recovery of empty cage fullerenes was 60% relative to the extract initially applied to the resin. Note that no or very little $Sc_3N@C_{80}$ had been bound to the resin, in accord with its greatly diminished reactivity relative to the other species in the complex mixture; however, see the discussion below. It is noteworthy that exposure of the extract to resin **2** and the recovery process resulted in a change in the ratio of C_{78} isomers as shown by comparison of Figure 3, parts a and c, in accord with the differing reactivities of the three known[28,29] isomers predicted by the calculations shown in Table 1.

No attempt was made in the present work to optimize the recovery process, but it should be noted that Rotello et al. achieved 48% recovery of bound C_{60} using their cyclopentadiene-functionalized resin[24] and 94% of bound C_{60} and 41% of bound C_{70} using an analogous cyclopentadiene-functionalized silica.[26]

D. Purification of Raw Soots. We then proceeded to study the raw soots themselves. As found with the extracts described above, the expected high degree of selectivity was observed in reactions with resin **2**.

1. $Lu_3N@C_{80}$. The raw soot from K–H arc treatment of graphite rods packed with Lu_2O_3 was applied as a powder to the top of a column of resin **2** and toluene; the column was flushed with toluene. As shown in Figure 5, mass spectral and HPLC analyses confirmed the identity and high purity of the effluent, the previously reported $Lu_3N@C_{80}$.[7a,7b] The high degree of selectivity is illustrated by the wide range of empty-cage fullerenes (C_{60}, C_{70}, C_{76}, C_{78}, C_{84}, etc.) and classical EMFs [$Lu_2@C_{82}$ and $Lu_2@C_{84}$, presumed by analogy with scandium analogues to possess tetraanionic cages, C_{82}^{-4} (unknown symmetry)[11b,30] and C_{84}^{-4} (D_{2d}, C_s, and C_{2v});[31] see Table 1] present in the soot that readily react with, and are trapped by, the cyclopentadiene-functionalized resin.

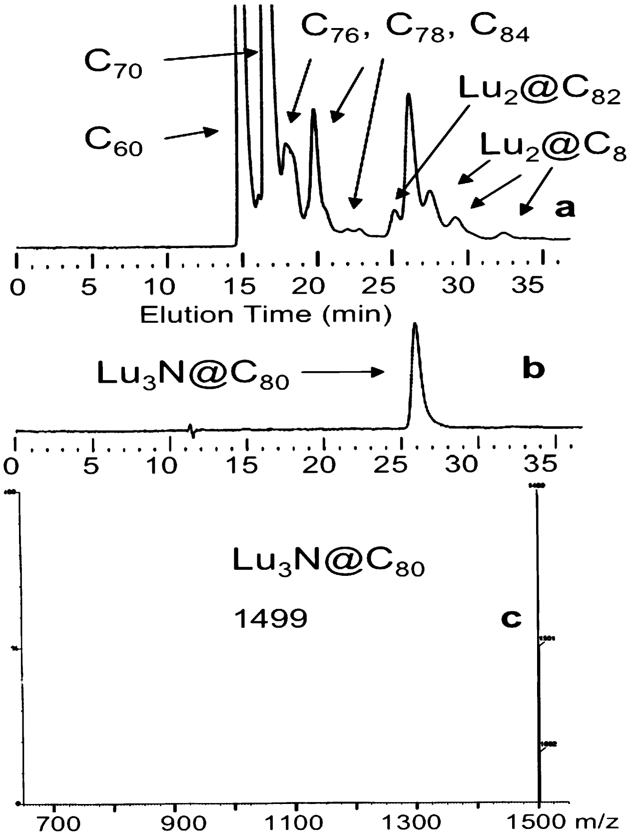

Figure 5. Purification of the raw soot to produce pure $Lu_3N@C_{80}$. (**a**) HPLC (Buckyclutcher column, toluene, 1 mL/min, detection at 390 nm) trace of the toluene extract of the soot produced in the presence of Lu_2O_3; the peaks correspond in approximate order of elution left to right: C_{60}, C_{70}, C_{76}, C_{78}, C_{84} (the latter three with ≥2 identified isomers), classical EMFs $Lu_2@C_{82}$, $Lu_3N@C_{80}$, and $Lu_2@C_{84}$ (≥2 isomers). (**b**) chemical ionization mass spectrum (negative ion) and (**c**) HPLC trace of eluted, pure $Lu_3N@C_{80}$.

2. $Sc_3N@C_{80}$. The collected raw soot from arc-vaporization of graphite/Sc_2O_3 was placed (as a powder) on top of a column packed with the cyclopentadiene-functionalized resin **2**/toluene and toluene was passed through the column. As was the case with the "scandium soot" extract described above (Figures 3 and 4) $Sc_3N@C_{80}$ was isolated in a relatively high state of purity,

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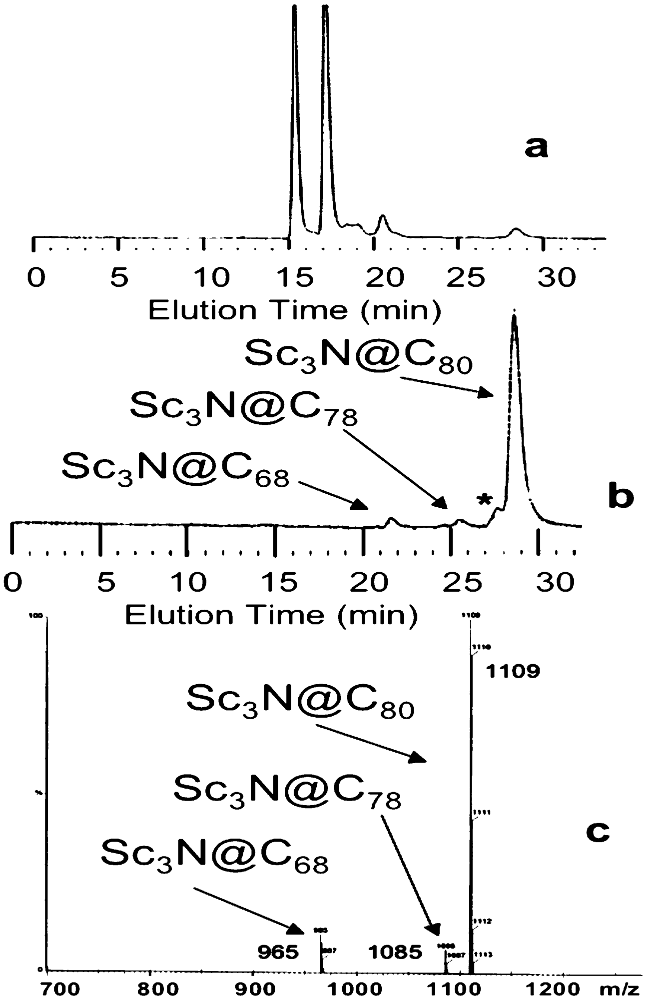

Figure 6. (**a**) HPLC (Buckyclutcher column, toluene, 1 mL/min, detection at 390 nm) trace of the toluene extract of "scandium soot"; (**b**) HPLC trace of the room-temperature toluene eluent from application of the raw soot to a column packed with cyclopentadiene-functionalized resin **2**; the three peaks noted correspond to TNT EMFs with different cage sizes and the peak with the asterisk is contamination introduced by the injector. (**c**) the chemical ionization mass spectrum (negative ion) of the eluent noted in (b) showing the presence of the three TNT EMFs.

containing the homologous TNT EMFs with smaller cage sizes, namely $Sc_3N@C_{68}$ and $Sc_3N@C_{78}$, in minor proportions (3.0 and 3.7%, respectively, by area from the chromatogram), as demonstrated by HPLC and mass spectrometric analyses (see Figure 6).

Assuming that, as in $Sc_3N@C_{80}$, six electrons are transferred to the cages, corresponding to $[Sc_3N]^{+6}@[C_{68}]^{-6}$ (D_3) and $[Sc_3N]^{+6}@[C_{78}]^{-6}$ (D_{3h}), the low chemical reactivity of these smaller TNT EMFs observed in the present work is consistent with the high kinetic stability deduced theoretically (Table 1).[11,12] Note, however, that these TNT EMF homologues are expected to be more reactive than $Sc_3N@C_{80}$ (Table 1).[12] Therefore, the extent of removal of these homologues is dependent on the details of the kinetic purification process. [Note that these homologues are not observed for the Lu_3N analogues, because the larger trimetallic nitride cluster is too large to fit the smaller C_{68} and C_{78} cages; hence, $Lu_3N@C_{80}$ is isolated as a pure single isomer (Figure 5).]

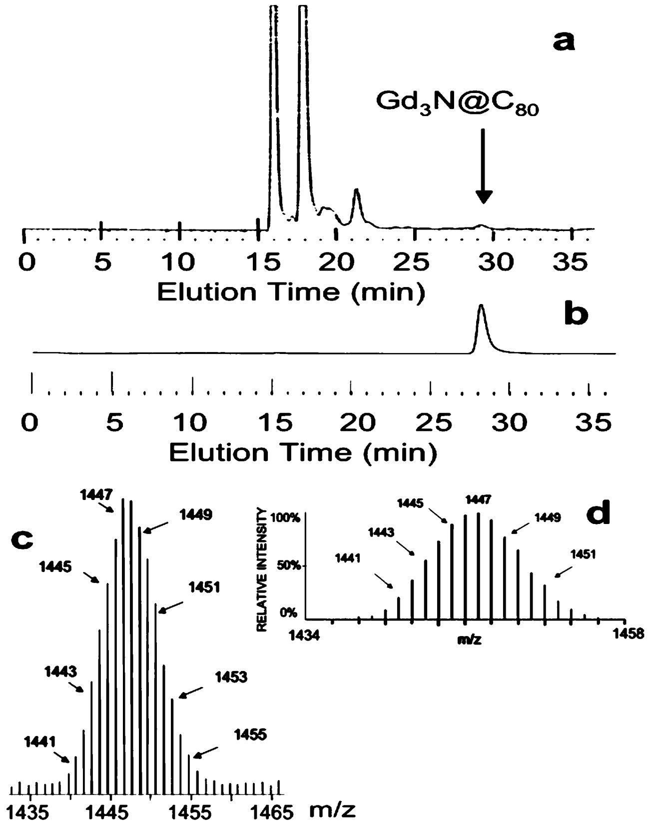

Figure 7. HPLC traces (Buckyclutcher column, toluene, 1 mL/min, detection at 390 nm) trace of **(a)** the toluene extract (Soxhlet, 4 h) of a soot mixture prepared from graphite rods packed with Gd_2O_3 and **(b)** purified $Gd_3N@C_{80}$ from toluene elution of the soot through a column packed with cyclopentadiene-functionalized resin **2** over a 20 h period; **(c)** the chemical ionization mass spectrum (negative ion) of the eluent noted in (b), identifying the pure TNT EMF and **(d)** the theoretical spectrum for $Gd_3N@C_{80}$ predicted on the basis of the natural isotopes of Gd, namely Gd^{152} (0.2%), Gd^{154} (2.1%), Gd^{155} (14.8%), Gd^{156} (20.6%), Gd^{157} (15.7%), Gd^{158} (24.8%) and Gd^{160} (21.8%).

For the three known[31] classical EMF $Sc_2@C_{84}$ isomers (C_s, C_{2v}, and D_{2d}) produced in this process the min BREs for the resultant $[C_{84}]^{-4}$ cages (Table 1) are indicative of higher reactivities than the TNT EMFs, in agreement with their higher experimentally observed reactivities with, and resultant trapping by, the cyclopentadiene-functionalized resin. Furthermore, it is noteworthy that the D_{5h} isomer of $Sc_3N@C_{80}$, which is observed as a longer retention time shoulder in HPLC analyses of samples purified chromatographically,[32] is not observed in these experiments (Figure 6). Furthermore, careful examination of Figure 3c indicates that this isomer reacted with the resin and was released upon treatment with maleic anhydride at 85 °C. This process comprises a separation of these two isomers.[33]

3. $Gd_3N@C_{80}$. The raw soot from K−H treatment of graphite rods packed with Gd_2O_3 was analogously treated by elution through a column of resin **2** with toluene at room temperature. Figure 7a displays the HPLC trace of the toluene extract of the soot, indicating the presence of the usual mixture of empty cage fullerenes, classical EMFs and TNT EMFs. The sample resulting

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[31] Inakuma, M.; Yamamoto, E.; Kai, T.; Wang, C.-R.; Tomiyama, T.; Shinohara, H.; Dennis, T. J. S.; Hulman, M.; Krause, M.; Kuzmany, H. *J. Phys. Chem. B.* **2000**, *104*, 5072−5077.

[32] (a) Duchamp, J. C.; Demortier, A.; Fletcher, K. R.; Dorn, D.; Iezzi, E. B.; Glass, T.; Dorn, H. C. *Chem. Phys. Lett.* **2003**, *375*, 655−659. (b) Krause, M.; Dunsch, L. *ChemPhysChem* **2004**, *5*, 1445−1449.

[33] Echegoyen and co-workers have recently reported an electrochemical method for separation of the I_h and D_{5h} isomers of $Sc_3N@C_{80}$: Elliott, B.; Yu, L.; Echegoyen, L. *J. Am. Chem. Soc.* **2005**, *127*, 10885−10888. The present protocol offers an alternative and complementary means of preparing the two pure isomers from the raw soot.

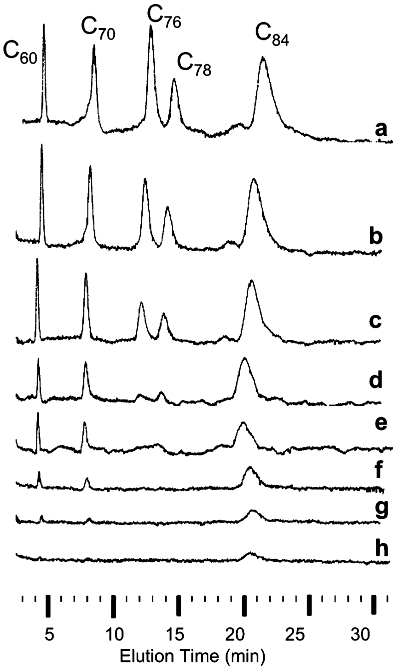

Figure 8. Kinetic stability of empty cage fullerenes with resin **2** at room temperature in toluene. (a) HPLC (PBB column, toluene, 2 mL/min, detection at 390 nm) trace of the initial empty cage fullerenes. HPLC traces of the solution 0.5 h after addition of (b) the first portion (4 mg), (c) the second portion (4 mg), (d) the third portion (10 mg), (e) the fourth portion (4 mg), (f) the fifth portion (4 mg), (g) the sixth portion (4 mg) and (h) the seventh portion (2 mg) of resin **2**.

from flushing the soot through the column was shown by HPLC (Figure 7b) and mass spectrometry (Figure 7c) to be pure $Gd_3N@C_{80}$. The experimental mass spectrum agrees well with the theoretically predicted one (Figure 7d).

E. Purification of Empty Fullerenes. The kinetic stability approach outlined here is not limited to purification of the TNT class of endohedral metallofullerenes, but can be extended to other fullerenes and presumably functionalized nanotubes. To demonstrate this, a small amount of resin **2** was added every 30 min to a stirred toluene solution of empty-cage fullerenes (C_{60}, C_{70}, C_{76}, C_{78} and C_{84}) at room temperature. The composition of the solution was monitored by HPLC. The results are shown in Figure 8. The removal of C_{76} and C_{78} is faster than removal of C_{60}, C_{70} and C_{84}. C_{76} and C_{78} disappear first and then C_{60} and C_{70}. When the other four empty cage fullerenes have been removed, some C_{84} remains. These results are consistent with the very low min BREs (high reactivities) for the known isomers of C_{76} (D_2),[28] C_{78} (C_{2v}),[29,34] C_{78} (C_{2v})[29,34] and C_{78} (D_3)[29,34] relative to C_{60} (I_h) and C_{70} (D_{5h}); see Table 1. Most of the eight known[34−40] neutral C_{84} isomers also have similar low min BREs, and are quite reactive; however, two other isomers have been isolated but not identified. Notably, however, a few isomers possess higher kinetic stability (e.g., D_{2-1} and T_d, Table 1), thereby potentially allowing them to be isolated in this manner; the unbound C_{84} noted in Figure 8, parts g and h, is presumed to be a mixture of these less reactive isomers.

Conclusions

High purity lanthanide trimetallic nitride endohedral metallofullerenes, $A_3N@C_{80}$ (A = lanthanide atom, e.g., Gd, Ho, Lu, Sc), can be obtained directly from as-prepared soots in a single facile step by taking advantage of their extraordinary kinetic chemical stability with respect to the Diels−Alder reaction with cyclopentadiene-functionalized resin. The present results indicate that it is possible to separate isomers of these TNT EMFs as well as various empty cage fullerenes. The thermal reversibility of the Diels−Alder reaction can, in principle, provide selective elution of fullerenes and endohedral metallofullerenes from the resin column as a function of temperature, flow rate, stoichiometry, and addition of competitive dienophiles. Moreover, complete removal of the bonded fullerenes would allow multiple cycles with the same resin, providing a purification approach that is scalable and consistent with Green Chemistry practices. We are currently pursuing these refinements of this protocol.

This new purification protocol has two advantages relative to the use of the HPLC method. First, the yields are higher by about 2-fold. This is due to the use of a lower temperature extraction solvent with reduced exposure to oxygen, hence decreased oxidative losses. In addition, repeated losses in the chromatographic process from multiple injections are avoided. A second major advantage is the time for obtention of pure endohedral trimetallic nitride fullerene samples, which is reduced from ca. 30 days to one (1) day.

Experimental Section

Materials and Methods. Graphite rods (99.9995% C, 6.15 mm × 152 mm) and graphite powder (99.9995% C) were obtained from Alfa Aesar. The graphite rods were drilled longitudinally to provide a 5/32" (4 mm) hole, which was packed with the metal oxide, Fe_xN and graphite powder (2−15 μm); the latter three components were mixed with a mortar and pestle and the graphite rod was packed with the resultant mixture using a cotton tip applicator, followed by the blunt end of the 5/32" drill bit. Scandium (III) oxide (Sc_2O_3, 99.999%), lutetium (III) oxide (Lu_2O_3, 99.995%), holmium (III) oxide (Ho_2O_3, 99.999%) and gadolinium (III) oxide (Gd_2O_3, 99.995%) were obtained from Stanford Materials Corporation. Iron nitride (99.9%, Fe_xN, $x = 2-4$) was obtained from Cerac Specialty Inorganic Chemicals. Merrifield's resin (chloromethylated styrene-1% divinylbenzene copolymer, 3.5−4.5 meq of Cl/g) and sodium cyclopentadienylide (2.0 M solution in tetrahydrofuran) were obtained from Sigma-Aldrich. C_{60} was obtained from Mer Corporation and used as received. A semipreparative Buckyclutcher column (10 x 250 mm, Regis Chemical Company) was used in high-pressure liquid chromatography (HPLC) for both analysis and purification. HPLC was also carried out on a β-(1-pyrenyl)ethyl silica (PYE) column (10 × 250 mm, Alltech Associates) and a pentabromobenzyloxypropyl silica (PBB) column (4.6 × 250 mm, Alltech Associates).

Cyclopentadiene-Functionalized Resin 2. A suspension of chloromethylated styrene-divinylbenzene copolymer (1 g) in toluene (200 mL) was cooled to −20 °C. To the stirred suspension, sodium cyclopentadienylide (16 mL of a 2.0 M solution in tetrahydrofuran, 32 mmol, ~8 equiv) was added dropwise. Then the mixture was stirred for 2 h at 20 °C and filtered; the beads were washed with toluene (600 mL) to give the dark brown cyclopentadiene-functionalized resin **2**.

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$Sc_3N@C_{80}$. $Sc_3N@C_{80}$was prepared by arc-vaporization of graphite rods packed with Sc_2O_3 (0.73 g, 5.3 mmol), Fe_xN (0.40 g) and graphite powder (1.00 g, total carbon ~2.5 g, 0.21 g at) in a K−H generator under a dynamic N_2 (20 mL/min)/He (~900 mL/min) atmosphere (at 300 Torr total pressure). The graphite rods were typically baked at ~1100 °C under N_2 for ~18 h just prior to arc-vaporization. A potential difference of 31 V was applied between the ends of the rods and maintained via electronic control. After each rod had been consumed (~45 min), the resulting soot was collected.

$Lu_3N@C_{80}$. $Lu_3N@C_{80}$ was prepared from graphite rods packed with Lu_2O_3 (0.85 g, 2.1 mmol) and Fe_xN (0.33 g) as outlined above for the Sc analogue.

$Gd_3N@C_{80}$. $Gd_3N@C_{80}$ was prepared from graphite rods packed with Gd_2O_3 (0.80 g, 2.2 mmol) and Fe_xN (0.33 g) as outlined above for the Sc analogue.

$Ho_3N@C_{80}$. $Ho_3N@C_{80}$ was prepared from graphite rods packed with Ho_2O_3 (0.80 g, 2.1 mmol) and Fe_xN (0.33 g) as outlined above for the Sc analogue.

Empty Cage Fullerenes. Empty cage fullerenes were prepared by arc-vaporization of graphite rods in a K−H generator under a dynamic He atmosphere (200 Torr). A potential difference of 31 V was applied between the ends of the rods and maintained via electronic control. After the rod had been consumed, the resulting soot was collected and extracted with toluene. Purification by HPLC (PBB column, toluene) afforded a mixture with similar amounts of C_{60}, C_{70}, C_{76}, C_{78}, and C_{84} (Figure 8a).

Purification of $Sc_3N@C_{80}$ Present in a Binary Mixture with C_{60}. A binary mixture of C_{60} (1.0 mg, 1.4 μmol) and $Sc_3N@C_{80}$ (1.0 mg, 0.90 μmol, purified as previously reported[4,5]) was applied as a toluene solution to the top of a glass column [13 × 25 mm, diameter (d) × height (h)] packed with 4 g of resin **2** (~16 mmol of reactive sites based on the starting chloromethylated resin capacity) in toluene. The column was flushed with toluene by gravity feed for 4 h. The resultant solution was concentrated and analyzed by HPLC (see SI).

Purification of $Gd_3N@C_{80}$ Present in a Binary Mixture with C_{60}. A binary mixture of C_{60} (1.0 mg, 1.4 μmol) and $Gd_3N@C_{80}$ (1.0 mg, 0.69 μmol purified as previously reported)[41] was applied as a toluene solution to the top of a glass column (13 × 20 mm, $d \times h$) packed with 4 g of resin **2** (~16 mmol of reactive sites based on the starting chloromethylated resin capacity) in toluene. The column was flushed with toluene by gravity feed for 4 h. The resultant solution was concentrated and analyzed by HPLC (see SI).

Purification of $Ho_3N@C_{80}$ Present in a Binary Mixture with C_{60}. A binary mixture of C_{60} (1.0 mg, 1.4 μmol) and $Ho_3N@C_{80}$ (1.0 mg, 0.68 μmol purified as previously reported)[42] was applied as a toluene solution to the top of a glass column (13 × 20 mm $d \times h$) packed with 4 g of resin **2** (~16 mmol of reactive sites based on the starting chloromethylated resin capacity) in toluene. The column was flushed with toluene by gravity feed for 4 h. The resultant solution was concentrated and analyzed by HPLC as shown in Figure 2.

Purification of $Sc_3N@C_{80}$ Soot Extract Using Resin 2 and Recovery of other Fullerenes. The raw soot from three graphite rods packed with Sc_2O_3 was collected and extracted in a Soxhlet device with toluene for 12 h, yielding 38.3 mg of mixed fullerenes and endohedral metallofullerenes after removing the solvent in vacuo; see Figure 4 for the mass spectrum of this material. This extract was redissolved in toluene and applied to a glass column (28 × 22 mm, $d \times h$) packed with ~20 g of cyclopentadiene-functionalized resin **2** (~180 mmol of reactive sites based on the starting chloromethylated resin capacity) in toluene. Toluene was flushed through by gravity feed (~6 mL/h) during 48 h. $Sc_3N@C_{80}$ was obtained after removing the solvent from the eluent (Figure 3b,c).

To study the reversibility of the covalent binding process, the column was wrapped with heating tape and a digital thermometer was inserted into the resin. At room temperature, two column volumes of toluene saturated with maleic anhydride were flushed through the column; no fullerenes were eluted. The column was then heated to 85 °C and kept at this temperature overnight. The solution in the column turned red, which indicated that the empty cage fullerenes had been released and replaced by the more the reactive dienophile, maleic anhydride. The column was flushed with toluene saturated with maleic anhydride at 85 °C over a 2 h period. The red solution was subsequently passed through a silica gel column to remove a small amount of maleic anhydride; removal of the solvent yielded 22.4 mg of recovered fullerenes; total recovery from extract: 23.4 mg, 61% (Figure 3c).

Purification of Raw $Lu_3N@C_{80}$ Soot Using Resin 2. The recovered soot (7.18 g) from two graphite rods packed with Lu_2O_3 was placed (as a powdery solid) on a glass column (38 × 25 mm, $d \times h$) packed with the cyclopentadiene-functionalized resin **2** (40 g, ~160 mmol of reactive sites based on the starting chloromethylated resin capacity) in toluene and toluene was passed through the column by gravity feed over a 20 h period. Pure $Lu_3N@C_{80}$ (9.0 mg, 0.21% yield based on Lu_2O_3 as the limiting reagent, 0.13% by mass of the soot) was isolated (Figure 5).

Purification of Raw $Sc_3N@C_{80}$ Soot Using Resin 2. The recovered soot (8.0 g) from two graphite rods packed with Sc_2O_3 was placed (as a powdery solid) on a glass column (38 × 25 mm, $d \times h$) packed with the cyclopentadiene-functionalized resin **2** (40 g, ~160 mmol of reactive sites based on the starting chloromethylated resin capacity) in toluene and toluene was passed through the column by gravity feed over a 20 h period. High purity $Sc_3N@C_{80}$ (11 mg, 0.19% yield based on C as the limiting reagent, 0.14% by mass of the soot) was isolated (Figure 6).

Purification of Raw $Gd_3N@C_{80}$ Soot Using Resin 2. The recovered soot (3.0 g) from one graphite rod packed with Gd_2O_3 was placed (as a powdery solid) on a glass column (28 × 22 mm, $d \times h$) packed with the cyclopentadiene-functionalized resin **2** (20 g, ~80 mmol of reactive sites based on the starting chloromethylated resin capacity) in toluene and toluene was passed through the column by gravity feed over a 20 h period. Pure $Gd_3N@C_{80}$ (0.30 mg, 0.014% yield based on Gd_2O_3 as the limiting reagent, 0.01% by mass of the soot) was isolated (Figure 7).

Purification of Empty Cage Fullerenes Using Resin 2. To a stirred solution of empty-cage fullerenes (C_{60}, C_{70}, C_{76}, C_{78}, and C_{84}) (1.0 mg, ~1.2 μmol total assuming equal masses) in 2 mL of toluene at room temperature, resin **2** was incrementally added every 30 min in the following sequence. The first and the second portions were 4 mg (~16 μmol of reactive sites based on the starting Merrifield resin capacity of 4.0 meq Cl/g) the third portion was 10 mg (~40 μmol of reactive sites based on the starting Merrifield resin capacity); the fourth, fifth, and sixth portions were also 4 mg each; the seventh portion was 2 mg. Total resin added: 32 mg (~128 μmol of reactive sites based on the starting Merrifield resin capacity of ~4.0 meq Cl/g). Before every addition of resin **2**, the solution was monitored by HPLC (Figure 8).

Acknowledgment. We thank NSF for support through awards CHE-043700 (H.C.D.) and DMR-0507083 (H.C.D., H.W.G.).

Supporting Information Available: HPLC traces of binary mixtures of C_{60} with $Gd_3N@C_{80}$ and $Sc_3N@C_{80}$ and the resultant purified $A_3N@C_{80}$ species; ultraviolet−visible absorption spectra of $Gd_3N@C_{80}$, $Ho_3N@C_{80}$, $Lu_3N@C_{80}$ and $Sc_3N@C_{80}$ purified using resin **2**; complete ref 13. This material is available free of charge via the Internet at http://pubs.acs.org.

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