An Efficient Method to Separate Sc$_3$N@C$_{80}$ I_h and D_{5h} Isomers and Sc$_3$N@C$_{78}$ by Selective Oxidation with Acetylferrocenium [Fe(COCH$_3$C$_5$H$_4$)Cp]$^+$

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Abstract: Based on the different oxidation potentials of endohedral fullerenes Sc$_3$N@C$_{80}$ I_h and D_{5h} and Sc$_3$N@C$_{78}$, an efficient and useful method that avoids HPLC has been developed for their separation. Selective chemical oxidation of the Sc$_3$N@D_{5h}-C$_{80}$ isomer and Sc$_3$N@C$_{78}$ by using an acetylferrocenium salt [Fe-(COCH$_3$C$_5$H$_4$)Cp]$^+$ followed by column chromatographic separation and reduction with CH$_3$SNa resulted in the isolation of pure Sc$_3$N@I_h-C$_{80}$, Sc$_3$N@C$_{78}$, and a mixture of Sc$_3$N@D_{5h}-C$_{80}$ and Sc$_3$N@C$_{68}$.

Keywords: endohedral metallofullerenes · geometric isomers · oxidation · reduction · scandium

Introduction

Trimetallic nitride endohedral metallofullerenes (TNT-EMFs) have attracted considerable attention mainly due to their potential applications,[1] as promising magnetic resonance imaging (MRI) contrast agents[2] candidates and in organic photovoltaics.[3] This is especially true for Sc$_3$N@I_h-C$_{80}$, because it is produced in high yields during arc production.[4] The icosahedral isomer of C$_{80}$ was initially observed for La$_2$@C$_{80}$.[5] Later, I_h symmetry cages were also observed for Ti$_2$@C$_{80}$,[6] Sc$_3$N@C$_{80}$,[4] Tb$_3$N@C$_{80}$,[7] and Lu$_3$N@C$_{80}$[8] among others.[1,9] The D_{5h} isomer of Sc$_3$N@C$_{80}$ (which constitutes approximately 10% of the arced sample), was isolated for the first time by high-performance liquid chromatography (HPLC) four years after the discovery of the I_h isomer.[10] The partial separation of the I_h and D_{5h} isomers was performed by HPLC using a PBB column (Phenomenex), followed by a BuckyPrep and a Buckyclutcher column, in series, resulting in very low yields.[10]

The interest to isolate the Sc$_3$N@D_{5h}-C$_{80}$ isomer is partly motivated by its higher reactivity compared to that of the I_h analogue; attributable to the difference between the HOMO–LUMO gaps of the isomers, with the D_{5h} possessing a smaller band gap.[10,11] In addition, the higher HOMO value of the Sc$_3$N@D_{5h}-C$_{80}$ isomer (−5.29 by DFT calculations[11] and −5.251 eV by cyclic voltammetry[12]), compared with that of the I_h isomer (−5.45 by DFT and −5.370 eV by cyclic voltammetry[12]), suggests it may exhibit interesting properties in bulk-heterojunction photovoltaic devices, and probably show better acceptor characteristics, even if the LUMO energies of both isomers are not significantly differ-

ent (−3.01 for Sc$_3$N@D_{5h}-C$_{80}$ and −2.91 eV Sc$_3$N@I_h-C$_{80}$).[11] HPLC is currently the only available technique to isolate the D_{5h} isomer[8,11,13,14] and is also the standard technique for the separation of metallofullerenes, empty-cage fullerenes, and structural isomers.[15] However, to purify metallofullerenes, a linear combination of two or three specialized HPLC columns is required,[10,16] or a recycling HPLC sequence with one of these specialized columns.[13] These procedures are not practical and are very time consuming, because large quantities of high-purity solvents are required. Additionally, the final isolated quantities are very small and the separation is not optimal.

Due to the inefficiency of the HPLC method, attempts have been made to find alternative chemical ways to separate TNT-EMFs and empty-cage fullerenes (ECFs) based on their reactivity. The first reported example to separate TNT-EMFs from ECFs in a single step used a cyclopentadiene-functionalized Merrifield resin.[17] A similar methodology was later reported by using eutectic 9-methylanthracene, which gave a mixture of empty fullerene adducts and unreacted TNT-EMFs (Sc$_3$N@C$_{78}$ and Sc$_3$N@C$_{80}$ isomers).[18] This method only allows the separation of Sc$_3$N@C$_{68}$ from the rest of the TNT-EMFs, but it is not an efficient method because Sc$_3$N@C$_{68}$ cannot be recovered. Another simple nonchromatographic method called "stir and filter approach" (SAFA) not only allows the separation of ECFs from TNT-EMFs, but also the separation of Sc$_3$N@C$_{68}$ and Sc$_3$N@C$_{78}$ from the Sc$_3$N@C$_{80}$ isomers.[19] The disadvantages of this method are: 1) time consuming (4 days to completely remove Sc$_3$N@C$_{68}$ and Sc$_3$N@C$_{78}$); 2) Sc$_3$N@C$_{68}$ and Sc$_3$N@C$_{78}$ cannot be recovered; and 3) it is not possible to separate Sc$_3$N@C$_{80}$ I_h from the D_{5h} isomer.

An alternative method based on the different oxidation potentials between the Sc$_3$N@C$_{80}$ I_h and D_{5h} isomers was reported to separate both isomers.[20] The separation was accomplished by using a silica-gel column and employing a chemical oxidizing agent, tris(*para*-bromophenyl)aminium hexachloroantimonate (TPBAH), to selectively oxidize

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Sc$_3$N@D_{5h}-C$_{80}$. Chromatographic separation gave pure icoso-hedral Sc$_3$N@C$_{80}$ after a single oxidative step that can be scaled up to any amount, but the method did not report the recovery of the oxidized D_{5h} isomer, which stays in the column.[20] A comparable method was reported by using a precipitation scheme utilizing Lewis acids that selectively complex TNT-EMFs, which allows the separation of the Sc$_3$N@I_h-C$_{80}$ isomer in gram quantities, but does not allow the separation of pure Sc$_3$N@D_{5h}-C$_{80}$.[21]

Therefore, there is no convenient and efficient method currently available to isolate the D_{5h} isomer of Sc$_3$N@C$_{80}$. Due to its unavailability, the chemistry of Sc$_3$N@D_{5h}-C$_{80}$ remains largely unexplored,[10,12,14,16] with just a few examples of its functionalization reported to date.[11,13] The work reported herein is focused on the scalable separation of the D_{5h} isomer from the I_h isomer, avoiding the use of HPLC techniques. The selective and complete separation of Sc$_3$N@C$_{80}$ I_h and D_{5h} isomers, as well as the first report of the separation of Sc$_3$N@C$_{78}$, was accomplished by using a chemical oxidizing scheme, based on the differences in the oxidation potentials of these three endohedral metallofuller-enes.

Results and Discussion

The separation of Sc$_3$N@C$_{80}$ I_h and D_{5h} is based on the different oxidation potentials of both isomers, which differ by 260 mV (Figure S1 and Table S1 in the Supporting Information). Because the first oxidation potential is very different for both isomers (Table 1), it was possible to find a suitable

Table 1. Anodic half-wave potentials [V] (versus Fc$^+$/Fc).

Compounds	$E_{1/2}$ ox$_1$
Sc$_3$N@C$_{80}$ (I_h)	0.59
Sc$_3$N@C$_{80}$ (D_{5h})	0.33
Sc$_3$N@C$_{78}$ (D_{3h})[25]	0.21
Sc$_3$N@C$_{68}$ (D_3)[26]	0.33
[Fe(η-C$_5$H$_4$COMe)Cp]$^{+}$[23]	0.27
TPBAH	0.71

oxidizing reagent that was able to selectively oxidize the D_{5h}. The selected oxidant was acetylferrocinium tetrakis-(pentafluorophenyl)boride ([Fe(COCH$_3$C$_5$H$_4$)Cp]-[TFAB]).[23,24] This cation-radical salt has an oxidation potential that is lower (0.27 V, Table 1) than that of the D_{5h} isomer (0.33 V, Table 1), and because Sc$_3$N@C$_{78}$ and Sc$_3$N@C$_{68}$ have lower oxidation potentials than Sc$_3$N@D_{5h}-C$_{80}$ (Table 1), an excess of the salt should oxidize all endohe-drals, except Sc$_3$N@I_h-C$_{80}$. The reason to change the oxidizing agent from the one previously reported[20] is because TPBAH has an oxidation potential that is higher than that of Sc$_3$N@I_h-C$_{80}$ (Figure S2 and Table S1 in the Supporting Information), therefore TPBAH can also oxidize the Sc$_3$N@I_h-C$_{80}$ isomer if added in excess.

To achieve the isomeric separation with [Fe(COCH$_3$C$_5$H$_4$)Cp][TFAB] and to compare with the reported results by using TPBAH,[20] two (12 mg) samples (Figure 1a and 2a) were dissolved in CS$_2$ (100 mL) by using
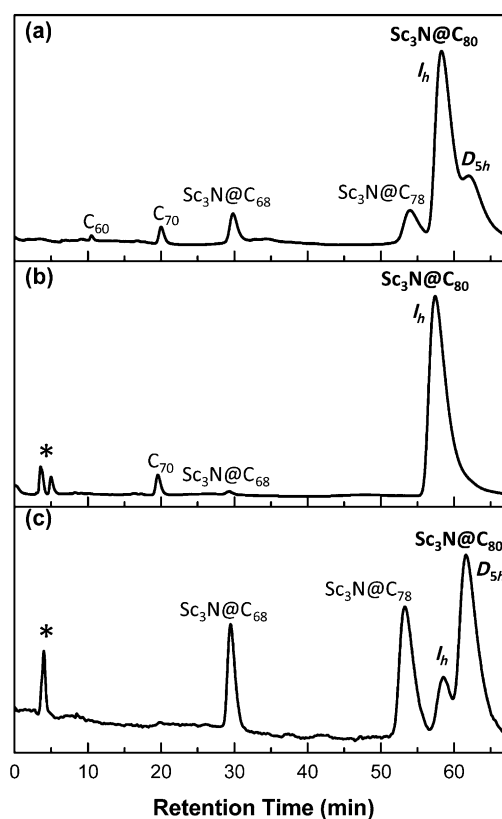

Figure 1. HPLC chromatograms of a) arc reactor sample (AS); b) pure Sc$_3$N@I_h-C$_{80}$ eluted after oxidation of AS with [Fe(COCH$_3$C$_5$H$_4$)Cp]-[TFAB]; c) mixture of Sc$_3$N@D_{5h}-C$_{80}$, Sc$_3$N@C$_{78}$, Sc$_3$N@C$_{68}$, and a small amount of Sc$_3$N@I_h-C$_{80}$ after eluting with the reductant CH$_3$SNa. Conditions: 5-PBB column 10ID × 250 mm, toluene (5 mL min^{-1}), detection at $\lambda = 320$ nm; peaks labeled with start belong to solvent.

sonication for 5 min. For simplicity, we define experiment A as the one employing [Fe(COCH$_3$C$_5$H$_4$)Cp][TFAB] and B for TPBAH. [Fe(COCH$_3$C$_5$H$_4$)Cp][TFAB] (10.54 mg) and TPBAH (9.41 mg) were dissolved in CH$_2$Cl$_2$ (3.5 mL and 6.5 mL, respectively) and added immediately to each fuller-ene sample. Both mixtures were sonicated for 90 min and then deposited in silica columns A (Scheme 1, cycle 1) and B. The amount of salt used for both experiments was calculated by using a deconvolution procedure (Cutter Version 5.0), to determine the area of Sc$_3$N@D_{5h}-C$_{80}$ in the HPLC chromatogram. The ratio used was Sc$_3$N@C$_{68}$/salt 1:4, Sc$_3$N@C$_{78}$/salt 1:3, and Sc$_3$N@D_{5h}-C$_{80}$/salt 1:3 for both oxidizing agents. The amount of C$_{60}$ and C$_{70}$ was not taken into account in the calculation of the amount of salt, because neither oxidizing agent is strong enough to oxidize the empty fullerenes.

The unoxidized compounds were eluted with CS$_2$, recovering 7.32 mg from column A and 3.55 mg from column B.
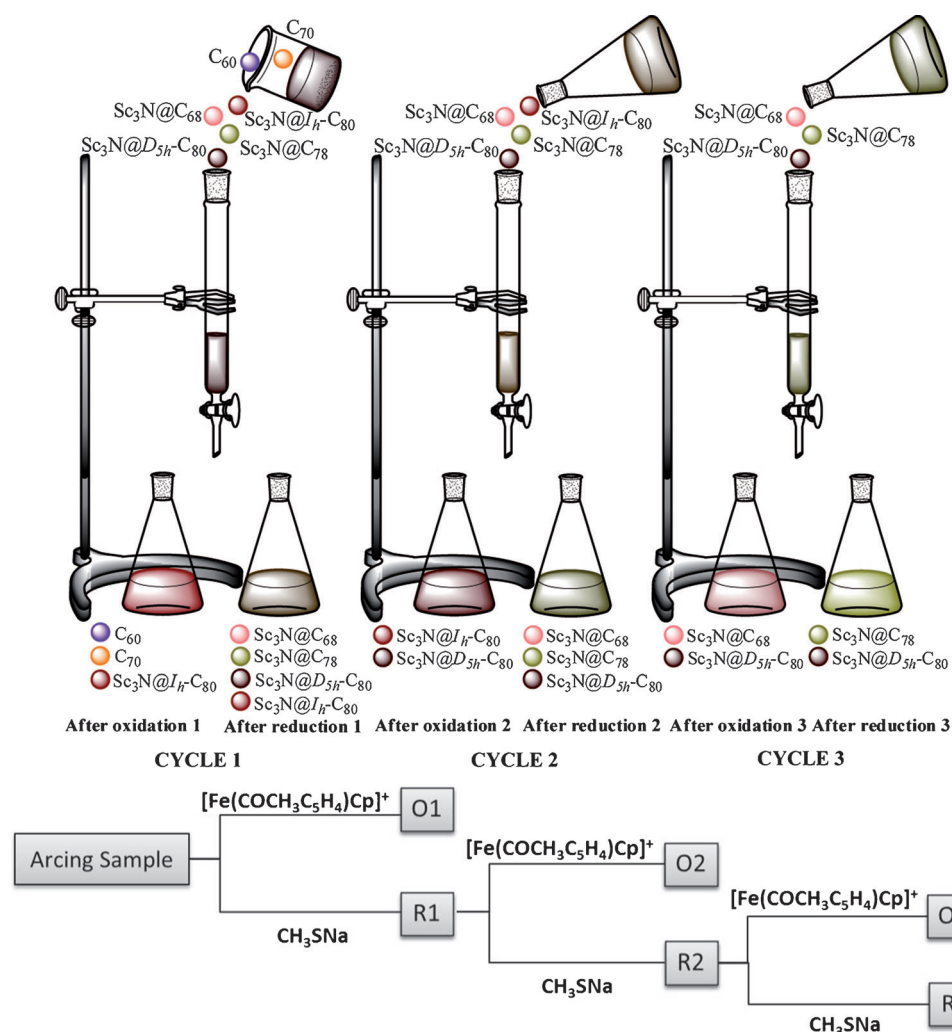
Scheme 1. Approach to purify Sc₃N@D_{5h}-C₈₀ by using [Fe(COCH₃C₅H₄)Cp][TFAB] as an oxidizing reagent and CH₃SNa as a reducing agent.

HPLC analysis of the two eluted fractions (Figures 1b and 2b, respectively) showed them to contain pure Sc₃N@C₈₀ I_h. The only notable difference between the results with both oxidizing agents is the recovered amount of Sc₃N@I_h-C₈₀.

To recover the oxidized fullerene-cation radicals adhered to the silica gel, CH₃SNa was then added as a reducing agent.[27] CH₃SNa (1.86 and 1.58 mg) was dissolved in methanol (2 and 1.8 mL, respectively) and added to the respective A and B columns. The amount of the CH₃SNa was calculated taking into account a ratio of 2:1 reducing agent/Sc₃N@C₆₈, Sc₃N@C₇₈, and Sc₃N@D_{5h}-C₈₀, then dissolved in the smallest amount of methanol possible to minimize changes in polarity of the mobile phase in the column.

After reduction, the fullerene mixture of both columns was eluted with CS₂, recovering 4.64 mg from column A and 4.74 mg from column B. HPLC analysis of the eluted fractions (Figures 1c and 2c) showed a mixture of Sc₃N@D_{5h}-C₈₀, Sc₃N@C₇₈, and Sc₃N@C₆₈, and a small amount of Sc₃N@I_h-C₈₀ from column A and a large amount of Sc₃N@I_h-C₈₀ in the case of B.

Although both procedures easily gave the pure I_h isomer, TPBAH gave a much lower yield due to its very high oxidation potential compared to that of Sc₃N@I_h-C₈₀ (Table 1). Any excess of the salt resulted in the oxidation of the I_h isomer as well. Almost 4 mg of the total sample remained in the column, which was impossible to recover even after multiple reduction attempts with CH₃SNa. The presence of a small amount of Sc₃N@I_h-C₈₀ in the eluent after CH₃SNa reduction of column A is probably due to the increased polarity of the solvent mixture, which decreases the solubility of the endohedral fullerenes,[15] thus leaving some Sc₃N@I_h-C₈₀ in the column after the elution of the first fraction.

To purify Sc₃N@D_{5h}-C₈₀, a series of oxidation and reduction cycles with [Fe(COCH₃C₅H₄)Cp][TFAB] and CH₃SNa were performed, which are summarized in Scheme 1.

To be able to completely remove Sc₃N@I_h-C₈₀, the second fraction obtained by reduction from column A (Figure 3a) was used to perform another oxidation/reduction cycle (Scheme 1, cycle 2). By using the same ratio of the salt with respect to Sc₃N@D_{5h}-C₈₀, Sc₃N@C₇₈, Sc₃N@C₆₈, and the fullerene sample (4.64 mg) was dissolved in CS₂ (50 mL) and
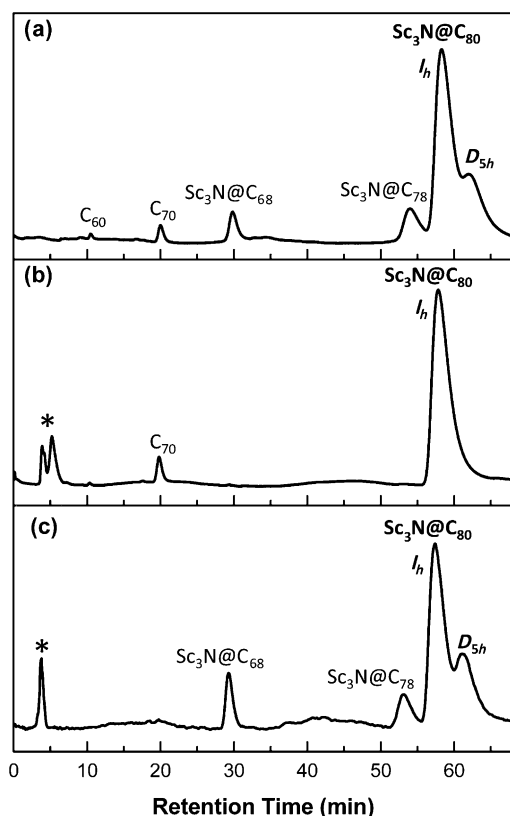
Figure 2. HPLC chromatograms of a) AS; b) pure Sc₃N@I_h-C₈₀ after eluting the oxidized AS with TPBAH; c) mixture of Sc₃N@I_h-C₈₀, Sc₃N@D_{5h}-C₈₀, Sc₃N@C₇₈, Sc₃N@C₆₈ after column reduction with CH₃SNa. Conditions: 5-PBB column 10ID×250 mm, toluene (5 mL min⁻¹), detection at $\lambda = 320$ nm; peaks labeled with star belong to solvent.

Figure 3. HPLC chromatograms of a) sample after reduction from the first silica-gel column; b) mixture of Sc₃N@I_h-C₈₀ and Sc₃N@D_{5h}-C₈₀ after oxidation with [Fe(COCH₃C₅H₄)Cp][TFAB]; c) mixture of Sc₃N@C₆₈, Sc₃N@C₇₈ and Sc₃N@D_{5h}-C₈₀ after reduction with CH₃SNa. Conditions: 5-PBB column, toluene (5 mL min⁻¹), detection at $\lambda = 320$ nm, peaks labeled with start belong to solvent.

[Fe(COCH₃C₅H₄)Cp][TFAB] (12.12 mg) in CH₂Cl₂ (3.6 mL) and added immediately to the fullerene sample, following the same procedure as already described. HPLC analysis after oxidation (Figure 3b) showed that Sc₃N@C₇₈ was completely oxidized as most of the Sc₃N@C₆₈ and Sc₃N@D_{5h}-C₈₀ (1.19 mg). The corresponding reduction was performed with CH₃SNa (2.10 mg) dissolved in methanol (2.5 mL). HPLC analysis of the eluted fraction with CS₂ (Figure 3c) showed the complete separation of Sc₃N@D_{5h}-C₈₀ from the I_h isomer, along with Sc₃N@C₇₈, and Sc₃N@C₆₈ (3.35 mg).

Finally, the second fraction obtained after reduction from the second column (Figure 4a) was used to do another oxidation and reduction cycle (Scheme 1, cycle 3) to separate Sc₃N@D_{5h}-C₈₀ and Sc₃N@C₆₈ from Sc₃N@C₇₈. By using a ratio of Sc₃N@C₇₈/salt 1:3, the fullerene sample (3.35 mg) was dissolved in CS₂ (40 mL) and [Fe(COCH₃C₅H₄)Cp]-[TFAB] (2.58 mg) in CH₂Cl₂ (1.1 mL). The same procedure as described previously was used. HPLC analysis after the oxidation step (Figure 4b) showed the complete separation of Sc₃N@D_{5h}-C₈₀ and Sc₃N@C₆₈ from Sc₃N@C₇₈. Sc₃N@D_{5h}-C₈₀ and Sc₃N@C₆₈ cannot be separated by this method, because they have almost identical oxidation potentials (Table 1). The corresponding reduction was performed with CH₃SNa (1.30 mg) dissolved in methanol (1.8 mL). HPLC
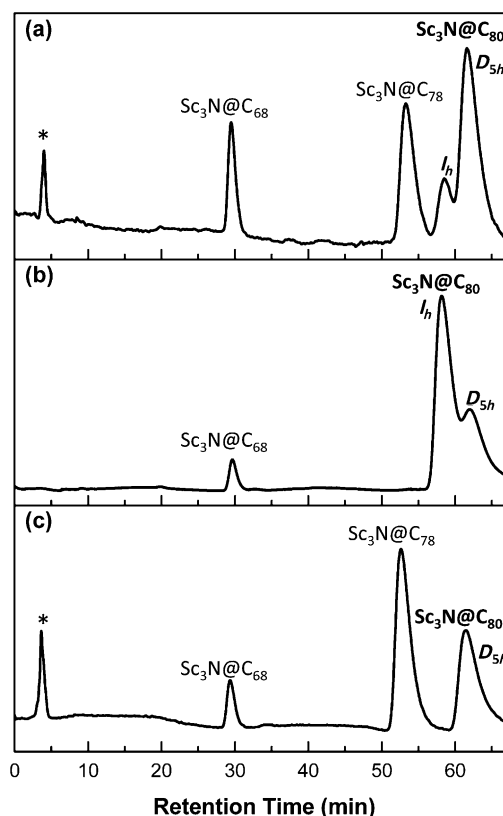
analysis of the eluted fraction with CS₂ (Figure 4c) showed Sc₃N@C₇₈ (major peak), as well as a small amount of Sc₃N@D_{5h}-C₈₀ and Sc₃N@C₆₈.

One of the advantages of this method over those reported[20,21] is that most of the Sc₃N@I_h-C₈₀ is recovered. In addition, it is not necessary to separate Sc₃N@C₆₈ and Sc₃N@C₇₈ by HPLC, and Sc₃N@D_{5h}-C₈₀ can be recovered.

Conclusion

An efficient and effective method to separate the I_h and D_{5h} isomers of Sc₃N@C₈₀ based on their oxidation potential differences has been developed. The complete and selective separation of the Sc₃N@D_{5h}-C₈₀ and Sc₃N@C₇₈ isomers from Sc₃N@I_h-C₈₀ by using acetylferrocinium [Fe(COCH₃C₅H₄)Cp]⁺ as an oxidizing agent and CH₃SNa as a reducing agent was accomplished.

Although Sc₃N@C₆₈ and Sc₃N@D_{5h}-C₈₀ cannot be separated based on the difference in the oxidation potential, the separation of the two can be made by using their different chemical reactivity.
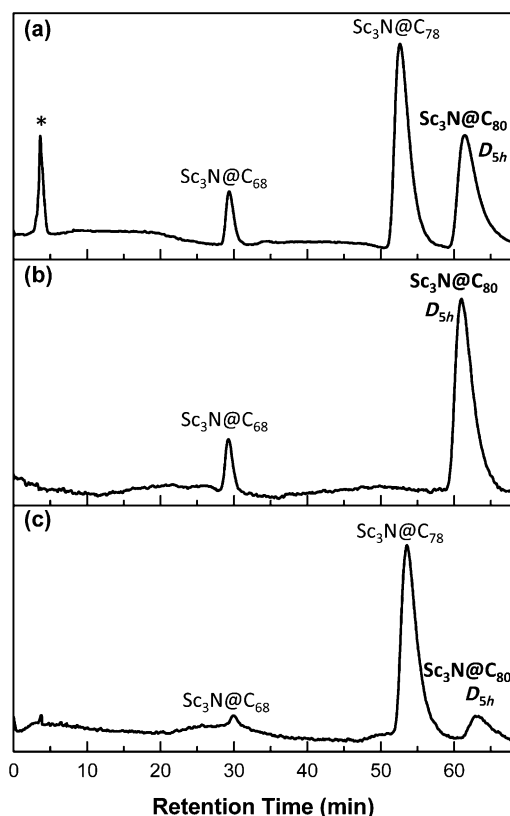
Figure 4. HPLC chromatograms of a) sample after reduction from the second silica-gel column; b) mixture of Sc$_3$N@D_{5h}-C$_{80}$ and Sc$_3$N@C$_{68}$ after oxidation with [Fe(COCH$_3$C$_5$H$_4$)Cp][TFAB]; c) mixture of Sc$_3$N@C$_{78}$ with a small amount of Sc$_3$N@D_{5h}-C$_{80}$ and Sc$_3$N@C$_{68}$ after reduction with CH$_3$SNa. Conditions: 5-PBB column, toluene (5 mL min^{-1}), detection at $\lambda = 320$ nm.

Experimental Section

The synthesis of TNT EMFs was conducted in an arc-discharge reactor by using ammonia as a "reactive-gas atmosphere", and graphite rods packed with Sc$_2$O$_3$ and graphite powder.[4] With this method, mainly metal nitride EMFs were obtained, with less than 5% empty fullerenes. HPLC analysis of the extract after washing with diethyl ether and acetone to remove polyaromatic hydrocarbons showed a mixture of six compounds, corresponding to C$_{60}$, C$_{70}$, Sc$_3$N@C$_{68}$, Sc$_3$N@C$_{78}$, and to an isomeric mixture of I_h and D_{5h} Sc$_3$N@C$_{80}$, with the latter showing as a trailing shoulder after the larger I_h isomer peak (Figure 1a). HPLC experiments were performed by using a 5-PBB column, which does not afford a complete separation of the two isomers in a single cycle.

Synthesis of the [Fe(COCH$_3$C$_5$H$_4$)Cp][TFAB] salt: To a stirring solution of [Fe(COCH$_3$C$_5$H$_4$)Cp] (213.05 mg, 0.93 mmol) in anhydrous diethyl ether (25 mL) at RT, a solution of AgBF$_4$ (201.00 mg, 1.03 mmol) in anhydrous diethyl ether (5 mL) was added by using a Schlenk line. After 0.5 h, the blue-green reaction mixture was evaporated to dryness in vacuum,[23] the residue was washed with anhydrous diethyl ether four times, 10 mL each, to remove excess of the unreacted starting material. The residue was extracted with anhydrous CH$_2$Cl$_2$ (100 mL). After filtration through a 0.2 μm PTFE syringe filter, the volume of the dark blue extract was dried in vacuum, giving 258.02 mg (87.82%) of the compound.

To a stirred solution of [Fe(COCH$_3$C$_5$H$_4$)Cp]BF$_4$ (94.90 mg, 0.30 mmol) in anhydrous CH$_2$Cl$_2$ (10 mL) at RT, a suspension of KTFAB (230.50 mg, 0.32 mmol) in anhydrous CH$_2$Cl$_2$ (8 mL) was added by using a Schlenk line. After 15 h, the blue-green reaction mixture was evaporated to dry-

ness in vacuum, and the residue was extracted with anhydrous diethyl ether (50 mL). After filtration through a 0.2 μm PTFE syringe filter, the volume of the green-blue extract was dried in vacuum, washed with anhydrous pentane, and kept in a desiccator (yield 209.30 mg, 75.13%).[24]

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