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A Facile Route to Metal Nitride Clusterfullerenes by Using Guanidinium Salts: A Selective Organic Solid as the Nitrogen Source

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Abstract: Using guanidinium salts **1** and **2** as the new nitrogen sources, metal nitride clusterfullerenes (NCFs) based on a variety of metals (Dy, Sc, Y, Gd, Lu, and mixed metals Sc/Dy, Sc/Gd, Sc/Lu, and Lu/Ce) have been synthesized based on a new "selective organic solid" (SOS) route. The synthesis of Dy-NCFs by using Dy/**1** was studied in detail, and the optimum molar ratio of **1**/Dy/C has been determined to be 2.5:1:10. For several representative metals such as Sc, Y, Gd, Dy, and Sc/Dy, we quantitatively compared the yield of $M_3N@C_{80}$ synthesized by the SOS route with the reported "reactive gas atmosphere" route, thereby indicating that the yield of $M_3N@C_{80}$ by using **1** could be comparable to that obtained by the reactive gas atmosphere route. Three other nitrogen sources (**3**–**5**) were also studied for comparison, which were mixed with Dy metal but did not result in the formation of Dy-NCF. A possible reaction scheme for the solid-state reaction of **1**, metal, and graphite is proposed. The SOS route appears to be a general route for the synthesis of NCFs that promises both high selectivity of NCFs and high reproducibility of the fullerene yield. Another advantages of the SOS route compared to the reported "trimetallic nitride template" (TNT) process and the reactive gas atmosphere route is that no additional heating pretreatment is needed, thus simplifying the procedure and being much more facile.

Keywords: fullerenes · guanidinium · metal nitride clusters · molecular structures · organic solids

Introduction

Among the endohedral fullerenes,[1] metal nitride clusterfullerenes (NCFs) are a special fullerene family with an encaged trimetallic nitride cluster.[2,3] In the past decade, NCFs have been attracting great interest because of the feasibility of tuning the trapped metal atoms and of stabilizing a large variety of cage sizes including different isomeric structures.[2–9] So far a number of homogenous NCFs have been synthesized and isolated, including $Sc_3N@C_{2n}$ ($2n = 68$, 70, 78, 80),[5,6] and $M_3N@C_{2n}$ ($78 \leq 2n \leq 88$ for M = Y, Gd, Tb, Dy, Ho, Er, Tm, Lu;[2,7–13] $80 \leq 2n \leq 96$ for M = Pr, Nd;[14–16] $86 \leq 2n \leq 96$ for M = La, Ce[16,17]). Furthermore, mixed-metal nitride clusterfullerenes (MMNCFs) such as $M_xSc_{3-x}N@C_{80}$ (M = Y, Ce, Nd, Gd, Tb, Dy, Er, Lu),[18–25] $DySc_2N@C_{76}$,[26] $Lu_2ScN@C_{68}$, $MSc_2N@C_{68}$ (M = Dy, Lu),[27] $Lu_xY_{3-x}N@C_{80}$,[28] $TiSc_2N@C_{80}$,[29] and $Lu_2CeN@C_{80}$[30] have been also isolated. Note that all of these NCFs were synthesized by two modified Krätschmer–Huffman direct current (DC)-arc-discharging methods: the "trimetallic nitride template" (TNT) process named by Dorn et al. in 1999,[5] and the "reactive gas atmosphere" route developed by Dunsch et al. in 2003,[3,31] with N_2 and NH_3 being the nitrogen source, respectively. Interestingly, although both N_2 and NH_3 are gaseous nitrogen sources, their effects on the yield of NCFs are remarkably different: for the TNT process the authors claimed to get a higher yield of NCFs in the soot extract ranging from 3 to 5%, whereas the reactive gas atmosphere route enables the NCFs to be the main product in the fullerene soot extract with selectivties up to 90%.[2,3,5,31] Given such a limitation on the synthesis methods of NCFs, an intriguing question is whether or not other nitrogen sources might be used in the DC-arc discharging method to synthesize NCFs.

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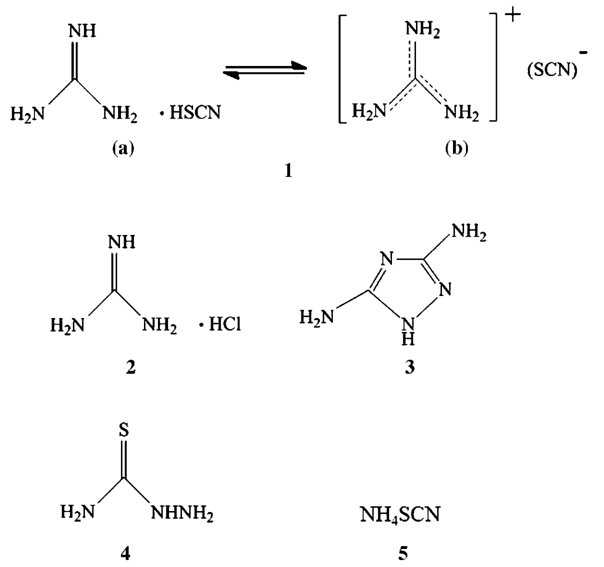
In the first stage of modifying the synthesis of NCFs, a solid nitrogen-containing inorganic compound, calcium cyanamide (CaNCN), which was added to the graphite mixture to the same extent as the metal content, was applied by Dunsch et al. in 2004.[3] According to the proposed reaction scheme for the solid-state reaction,[3] the generation of gaseous nitrogen as used in the TNT process was expected, whereas there is no need of any amount of oxygen in this modified method. Clearly this "inorganic solid nitrogen" source causes a strong increase in the selectivity of the NCFs as confirmed by the fact that the $Sc_3N@C_{80}$ NCF was synthesized as the main product of the fullerene soot with a selectivity ranging from 3 to 42%.[3] However, the disadvantage of this inorganic solid nitrogen route was the low reproducibility of the fullerene yield, and this might be due to traces of water and/or hydrocarbons in the raw material.[3] As a result, this inorganic solid nitrogen route was not widely applied in the synthesis of other NCFs and is yet to be optimized.

With the strong motivation of developing new synthesis methods for NCFs to simplify the procedure and/or to increase the selectivity of the NCFs, herein we report a new and facile route to the synthesis of NCFs by using guanidinium salt as the new nitrogen source. A systematic study on different synthesis routes of NCFs based on different nitrogen sources, various metals (Dy, Sc, Y, Gd, Lu), and mixed metals (Sc/Dy, Sc/Gd, Sc/Lu, and Lu/Ce) was carried out, thus validating the applicability of the guanidinium salt as an effective nitrogen source. The synthesis conditions of Dy-NCFs by using guanidinium thiocyanate were optimized, and the yields of $M_3N@C_{80}$ are compared with that obtained from the reported reactive gas atmosphere route. Furthermore, we carried out several reference syntheses by using other nitrogen-containing solids, which, however, did not result in the formation of NCFs. A plausible explanation is proposed to interpret these results. In recognition of the distinct selectivity of the organic solids towards the formation of NCFs, we name this new method the "selective organic solid" (SOS) route.

Results and Discussion

Synthesis of Dy-NCFs by using different nitrogen-containing solids: In light of the high content of nitrogen in the molecules of calcium cyanamide (CaNCN) and NH_3 used in the "inorganic solid nitrogen" and "reactive gas atmosphere" routes,[2,3] respectively, in this study we selected four organic solids in which the content of nitrogen atom in the molecule is even higher,[32] including two guanidinium salts (guanidinium thiocyanate ($CH_5N_3{\cdot}HSCN$, **1**) and guanidinium hydrochloride ($CH_5N_3{\cdot}HCl$, **2**)), 3,5-diamino-1,2,4-triazole ($C_2H_5N_5$, **3**), and thiosemicarbazide (CH_5N_3S, **4**) (see Scheme 1). In addition, an inorganic salt, ammonium thiocyanate (NH_4SCN, **5**), was also selected because its cation NH_4^+ is derived from the gaseous NH_3 and there is no metal cation.



Scheme 1. Molecular structures of the nitrogen-containing solids studied in this work. Guanidinium thiocyanate (**1**; a) and its resonance structure (b); guanidinium hydrochloride (**2**); 3,5-diamino-1,2,4-triazole (**3**); thiosemicarbazide (**4**); and ammonium thiocyanate (**5**).

Figure 1 presents the HPLC profiles of the fullerene extracts obtained from the DC-arc discharge of Dy mixed with the five nitrogen-containing solids **1**–**5** under identical arc-discharging conditions, which also includes those of Dy_2O_3 with the addition of NH_3 (20 mbar; curve c) and pure Dy_2O_3 without the addition of any nitrogen source (curve d) for comparison. Clearly, for the Dy/guanidinium salt (Dy/**1** and Dy/**2**) extracts (curves a and b, Figure 1I), the fractions at $t_R > 32.6$ min are dominant in the fullerene extracts, for which the sum abundance is overwhelmingly higher than those of the empty fullerenes C_{60} and C_{70} ($t_R = 9.7$ and 15.2 min, respectively). Clearly this is very similar to the Dy_2O_3/NH_3 extract (curve c) for which the abundance of the corresponding fractions reaches up to 98% of all of the fullerenes.[7] This result suggests that, similar to the case of Dy_2O_3/NH_3 extract, a large Dy-NCF family ($Dy_3N@C_{2n}$, $39 \leq n \leq 44$)[7] is successfully synthesized in the Dy/guanidinium salt (**1** and **2**) extracts. In particular, the most abundant fraction (A) with $t_R = 33.4$ min in the Dy_2O_3/NH_3 extract, which has been assigned to $Dy_3N@C_{80}$ (I, I_h) according to our earlier study,[7,9] is also most abundant in Dy/**1** and Dy/**2** extracts (see Figure 1II), thereby indicating that $Dy_3N@C_{80}$ (I, I_h) is synthesized in Dy/**1** and Dy/**2** extracts at the highest yield, which is slightly lower than that obtained in the Dy_2O_3/NH_3 extract.[7]

Some other nitrogen-containing organic solids were then studied for comparison. Compared to **1** and **2**, compound **3** has a much higher nitrogen content[32] and there are two conjugated C=N bonds within the triazole ring, whereas **1** and **2** have resonance-stabilized C=N bonds. Compound **4** was studied because its nitrogen content is quite comparable to that in **1** and **2**. In contrast, the HPLC profiles of Dy/**3** and Dy/**4** extracts as shown in Figure 1III (curves e and f)

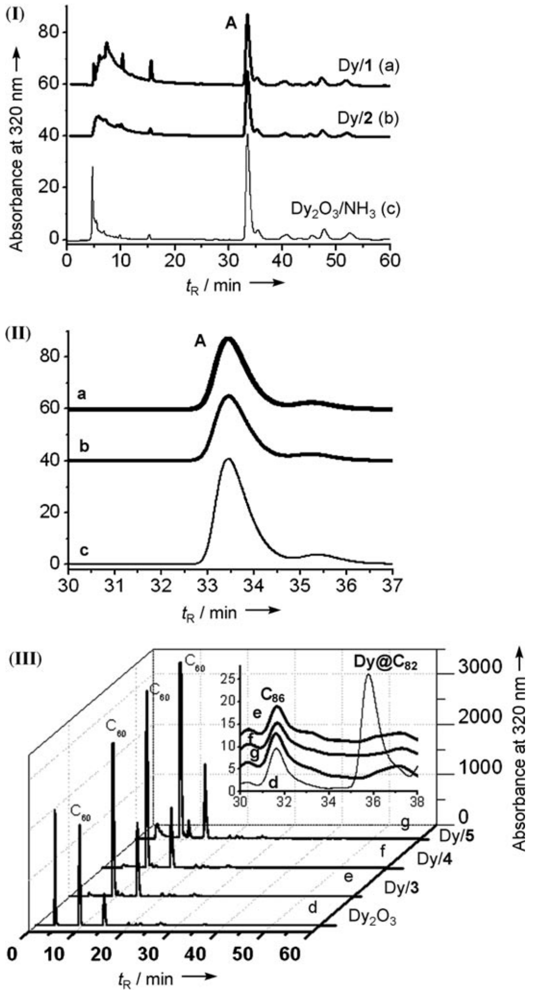


Figure 1. I–III) HPLC chromatograms of the Dy/**1**–**5** extracts obtained under identical arc-discharging conditions in comparison with those of Dy$_2$O$_3$/NH$_3$ and pure Dy$_2$O$_3$ extracts (linear combination of two 4.6×250 mm Buckyprep columns; flow rate 1.6 mL min^{-1}; injection volume 100 µL; toluene as eluent (mobile phase); 40 °C). II) The enlarged chromatographic region of 30–37 min of I. Fraction A represents Dy$_3$N@C$_{80}$ (I, I_h). The peak with t_R at 9.6 and 14.7 min corresponds to C$_{60}$ and C$_{70}$, respectively (t_R: retention time).

are dramatically different to those of Dy/**1**, Dy/**2**, and Dy$_2$O$_3$/NH$_3$ extracts, with the main difference observed in the region of $t_R > 30$ min: in Dy/**3** and Dy/**4** extracts there are no clear peaks at $t_R = 33.4$ min, and the intense peak at $t_R = 31.6$ min (which is assigned to C$_{86}$[33]) is not detected in Dy/**1**, Dy/**2**, and Dy$_2$O$_3$/NH$_3$ extracts at all (see inset of Figure 1III). On the other hand, it is also evident that a dramatic difference in the yield of empty fullerenes C$_{60}$ and C$_{70}$ among the Dy/**1** to Dy/**4** extracts exists. In Dy/**3** and Dy/**4** extracts, C$_{60}$ and C$_{70}$ are overwhelmingly dominant (≈99 %), and the higher empty fullerenes (e.g., C$_{76}$, C$_{78}$, C$_{84}$) are also detected with reasonable yield. However, in Dy/**1**, Dy/**2**, and Dy$_2$O$_3$/NH$_3$ extracts the abundance of C$_{60}$ and C$_{70}$ is much lower than Dy$_3$N@C$_{2n}$ NCFs.[7]

Ammonium thiocyanate (NH$_4$SCN, **5**) composed of NH$_3$ and HSCN was then studied for comparison with the gaseous NH$_3$ used in the reactive gas atmosphere route.[2,3,7] The similar result as for Dy/**3** and Dy/**4** extracts was obtained for the Dy/**5** extract (curve g, Figure 1III), thereby indicating the dominant formation of empty fullerenes C$_{60}$ and C$_{70}$ although the peak at $t_R = 33.4$ min is missing. Interestingly, the HPLC profiles of Dy/**3** to Dy/**5** extracts are almost identical in terms of the yield of empty fullerenes including C$_{86}$, thus suggesting that their effects on fullerene formation are very close. Besides, compared to the pure Dy$_2$O$_3$ extract without the addition of any nitrogen source (curve d, Figure 1III), Dy/**3** to Dy/**5** extracts are quite similar in terms of the yield of empty fullerenes including C$_{86}$. However, there is a distinct difference between the pure Dy$_2$O$_3$ and Dy/**3** to Dy/**5** extracts: in the pure Dy$_2$O$_3$ extract, an intense peak at $t_R = 35.8$ min, which is assigned to Dy@C$_{82}$ and has a higher intensity than C$_{86}$,[33] is clearly missing in Dy/**3** to Dy/**5** extracts (see inset of Figure 1III), thereby suggesting that the formation of endohedral metallofullerenes such as Dy@C$_{82}$ is significantly suppressed by **3** to **5**. This conclusion is further confirmed by the mass spectroscopic analysis as discussed below.

Dy/**1** to Dy/**5** extract mixtures were measured by laser desorption time-of-flight mass spectroscopy (LD-TOF MS). The results are presented in Figure 2 and include those of Dy$_2$O$_3$/NH$_3$ (curve c) and pure Dy$_2$O$_3$ (curve d) extracts. Clearly, the MS spectra of Dy/**1** and Dy/**2** mixtures (curves a and b) are very similar to that of Dy$_2$O$_3$/NH$_3$ except for the difference of the relative intensity of the MS peaks. In particular, the MS peaks at m/z 1461.5, which is assigned to Dy$_3$N@C$_{80}$,[7] are clearly detected in Dy/**1** and Dy/**2** mixtures

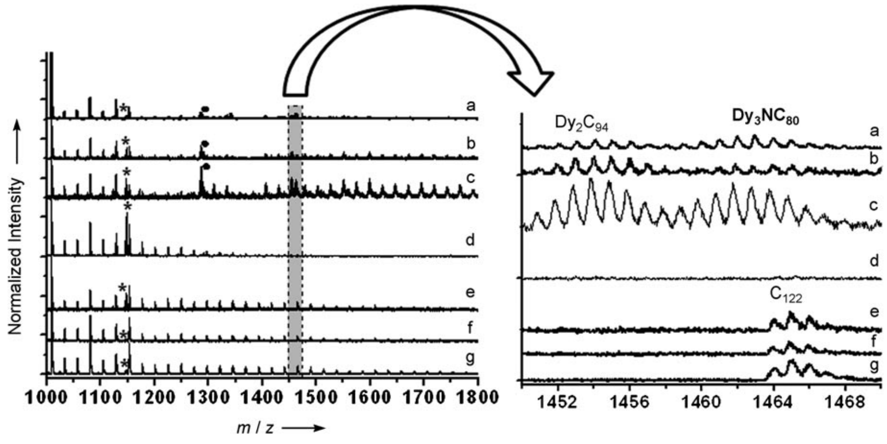


Figure 2. LD-TOF MS of the a) Dy/**1**, b) Dy/**2**, c) Dy$_2$O$_3$/NH$_3$, d) Dy$_2$O$_3$, e) Dy/**3**, f) Dy/**4**, g) Dy/**5** extract mixtures (negative-ion mode). The inset shows the enlarged spectroscopic region of m/z 1450–1470. The asterisks and filled circles represent Dy@C$_{82}$ and Dy$_2$@C$_{80}$, respectively.

(see inset of Figure 2), thus indicating that $Dy_3N@C_{80}$ has been successfully synthesized. Further analysis of the MS spectra of Dy/**1** and Dy/**2** mixtures reveals the formation of a large Dy-NCF family ($Dy_3N@C_{2n}$, $38 \leq n \leq 49$), as found in the Dy_2O_3/NH_3 extract.[7] Combined with the above HPLC analysis of Dy/**1** and Dy/**2** extracts in comparison with the Dy_2O_3/NH_3 extract, this result confirms unambiguously the successful synthesis of Dy-NCFs ($Dy_3N@C_{2n}$, $38 \leq n \leq 49$)[7] by using guanidinium salts **1** and **2** as the new nitrogen sources.

On the contrary, the MS spectra of Dy/**3** to Dy/**5** extract mixtures (curves e–g) are again dramatically different to those of Dy/**1**, Dy/**2**, and Dy_2O_3/NH_3 mixtures and exhibit the formation of a series of empty fullerenes up to C_{148} (*m*/*z* 1776) as the major MS peaks. The MS peaks of $Dy_3N@C_{80}$ (*m*/*z* 1461.5) are not detected in Dy/**3** to Dy/**5** mixtures at all (see inset of Figure 2), thereby indicating no formation of Dy-NCF in the Dy/**3** to Dy/**5** mixture. In addition, a comparison of the MS spectra of Dy/**3** to Dy/**5** mixtures with that of pure Dy_2O_3 extract reveals that the intensity of the characteristic MS peak of $Dy@C_{82}$ (*m*/*z* 1146.5) is dramatically weakened and another MS peak of $Dy_2@C_{80}$ (*m*/*z* 1285) is completely undetected in Dy/**3** to Dy/**5** mixtures. Since it is well known that $Dy@C_{82}$ and $Dy_2@C_{80}$ are the most abundant endohedral metallofullerenes in pure Dy_2O_3 extract, this result suggests that their formation is significantly suppressed in Dy/**3** to Dy/**5** mixtures, and this conclusion is in good agreement with the HPLC analysis of Dy/**3** to Dy/**5** mixtures as discussed above.

In summary, we have selected five nitrogen sources **1**–**5** mixed with Dy metal in an attempt to synthesize Dy-NCFs. Based on the detailed HPLC and MS analysis, we find that only guanidinium salts **1** and **2** are successful in the formation of Dy-NCFs. Contrarily, **3**, **4**, and **5** did not result in any formation of Dy-NCF and instead suppressed significantly the formation of conventional endohedral metallofullerenes such as $Dy@C_{82}$ and $Dy_2@C_{80}$. The possible reason why **1**–**5** differ in the formation of NCF is discussed below.

Optimization of the synthesis conditions of Dy-NCFs by using guanidinium salt 1: Since both guanidinium salts **1** and **2** can be successfully applied in the formation of Dy-NCFs, their synthesis conditions are to be optimized. According to the HPLC peak intensity of $Dy_3N@C_{80}$ (I, I_h) (fraction A, $t_R = 33.4$ min), the yield of $Dy_3N@C_{80}$ (I, I_h) of Dy/**2** extract is quite comparable to that of Dy/**1** extract (see Figure 1II). As the content of nitrogen atom in **2** is comparable to that in **1**,[32] the guanidinium cation $(C(NH_2)_3)^+$ is the crucial nitrogen source, whereas the anions SCN^- and Cl^- (see Scheme 1) have little effect on the formation of Dy-NCFs. Accordingly, we focus on optimizing the synthesis conditions using **1** by varying the molar ratio of **1**/Dy with a fixed molar ratio of Dy/C (1:10) according to the previous study.[7] Figure 3 compares the HPLC profiles of a series of fullerene extracts obtained under different molar ratios of **1**/Dy ranging from 0.5:1 to 3:1, thus indicating the strong dependence of the yield of $Dy_3N@C_{80}$ (I, I_h) in fraction A as well as the empty fullerenes (mainly C_{60} and C_{70}) on the molar ratios of **1**/Dy.

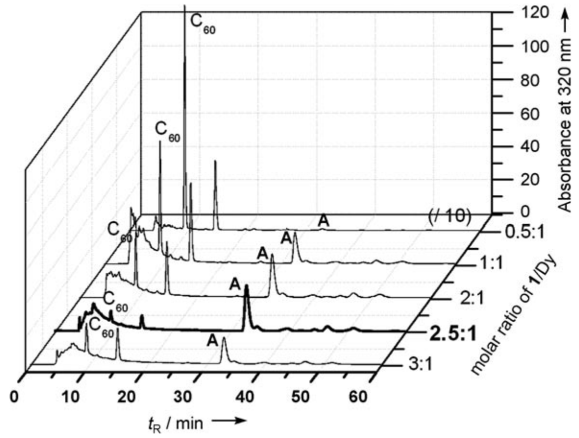


Figure 3. HPLC chromatograms of the Dy/**1** fullerene extracts obtained with different molar ratio of **1**/Dy (linear combination of two 4.6 × 250 mm Buckyprep columns; flow rate 1.6 mL min⁻¹; injection volume 100 μL; toluene as eluent (mobile phase); 40 °C). Fraction A represents $Dy_3N@C_{80}$ (I, I_h).

Figure 4a demonstrates the dependence of the HPLC peak intensity of $Dy_3N@C_{80}$ (I, I_h) (fraction A), which is obtained from Figure 3 and is proportional to the yield of $Dy_3N@C_{80}$ (I, I_h), on the molar ratios of **1**/Dy. In addition, the relative intensity of $Dy_3N@C_{80}$ (I, I_h) to C_{60} is also included as the ratio of their relative yield (curve b). The production of empty fullerenes (mainly C_{60} and C_{70}) is dominant at relatively low molar ratios of **1**/Dy from 0.5:1 to 1:1, whereas the production of $Dy_3N@C_{80}$ (I, I_h) becomes competitive with that of C_{60} and C_{70} when the molar ratio of **1**/Dy increases to 2:1. When the molar ratio of **1**/Dy is 2.5:1, the production of $Dy_3N@C_{80}$ (I, I_h) is apparently dominant compared to C_{60} and C_{70}. However, a further increase of the molar ratio of **1**/Dy to 3:1 results in a clear decrease of the $Dy_3N@C_{80}$ (I, I_h) yield and a simultaneous increase of the yield of C_{60} and C_{70}. Therefore, the optimum molar ratio of **1**/Dy is determined to be 2.5:1. The relative yield of

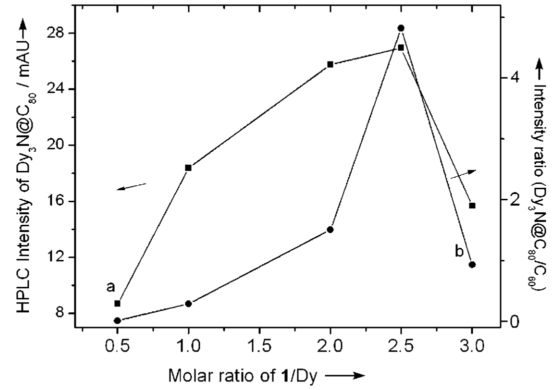


Figure 4. Effect of the molar ratio of **1**/Dy on the HPLC peak intensities of a) $Dy_3N@C_{80}$ (I, I_h) and b) its relative yield to C_{60}.

$Dy_3N@C_{80}$ (I, I_h) to C_{60} follows the same trend and also exhibits the maximum (≈ 4.8) at the ratio of **1**/Dy = 2.5:1 (see curve b). When the molar ratio of **1**/Dy increases to 3:1, the relative yield of $Dy_3N@C_{80}$ (I, I_h) to C_{60} decreases dramatically.

It should be noted that, using **1** as the nitrogen source, in addition to the selective formation of Dy-NCFs we found that the metal sulfide clusterfullerene $Dy_2S@C_{82}$ formed simultaneously along with the Dy-NCFs. This phenomena was further studied by varying the metal to Sc, Y, and Lu, thus leading to the discovery of a new type of sulfur-containing clusterfullerenes $M_2S@C_{82}$ (M = Sc, Y, Dy, and Lu) despite the relatively low yield (e.g., the relative yield of $Sc_2S@C_{82}$ to $Sc_3N@C_{80}$ (I) is approximately 1:150 on the basis of the integrated area of the corresponding peaks in the chromatogram) as described recently.[34]

Synthesis of NCFs based on other metals by using 1 and comparison with use of NH_3: With the optimum molar ratio of **1**/Dy/C determined to be 2.5:1:10, we extended the study to other metals M including Sc, Y, Gd, and Lu, and mixed metals Sc/Dy, Sc/Gd, Sc/Lu, and Lu/Ce, which were mixed with **1** (molar ratio of **1**/M is fixed at 2.5:1 (M = Sc, Gd, Y, Lu) and 2.5:1:1 (M = Sc/Dy, Sc/Gd, Sc/Lu, Lu/Ce).[20,26,27,30,34] Figure 5 presents the HPLC profiles of the fullerene extracts obtained from Gd/**1** (I), Y/**1** (II), Sc/**1** (III), and Sc/Dy/**1** (IV) extracts. Clearly the chromatogram of M/**1** extract is very similar to that of M_2O_3/NH_3 extract in terms of the fraction distribution and the comparable peak intensity of the most abundant fraction A. The MS spectroscopic analysis of each extract confirms the close similarity of M/**1** to the M_2O_3/NH_3 extract according to the main products formed (Figure 6). Therefore, these results validate the applicability of the present method of using **1** as the nitrogen source to synthesize NCFs based on a variety of metals.

The yield of fraction A obtained from the M/**1** extract (see Figure 5) has been compared with that obtained from the corresponding M_2O_3/NH_3 extract. Given that the peak width of fraction A is the same for both extracts, the comparison of the yield of fraction A is simplified by comparing the HPLC peak intensity. Shown in Figure 7 is the quantitative comparison of the peak intensity of fraction A obtained from the corresponding M/**1** and M_2O_3/NH_3 extracts (M = Gd, Dy, Y, Sc, Sc/Dy), thus indicating the strong metal dependence. Interestingly, although the intensity of fraction A obtained from Dy/**1**, Y/**1**, and Sc/**1** is clearly lower than those obtained from the corresponding M_2O_3/NH_3 extracts, for Sc/Dy/**1** the intensity of fraction A becomes quite comparable to that obtained from $Sc_2O_3/Dy_2O_3/NH_3$ extract, whereas the situation is reversed for Gd/**1** and Gd_2O_3/NH_3 extracts, thus suggesting that the yield of $Gd_3N@C_{80}$ may be enhanced by replacing NH_3 with **1** as the nitrogen source. This enhancement is particularly significant considering the potential application of Gd-based endohedral fullerenes as new contrast agents in magnetic resonance imaging (MRI).[2,35] The above results suggest that the yield of $M_3N@C_{2n}$ obtained from using **1** could be comparable to that obtained from the reactive gas atmosphere route.

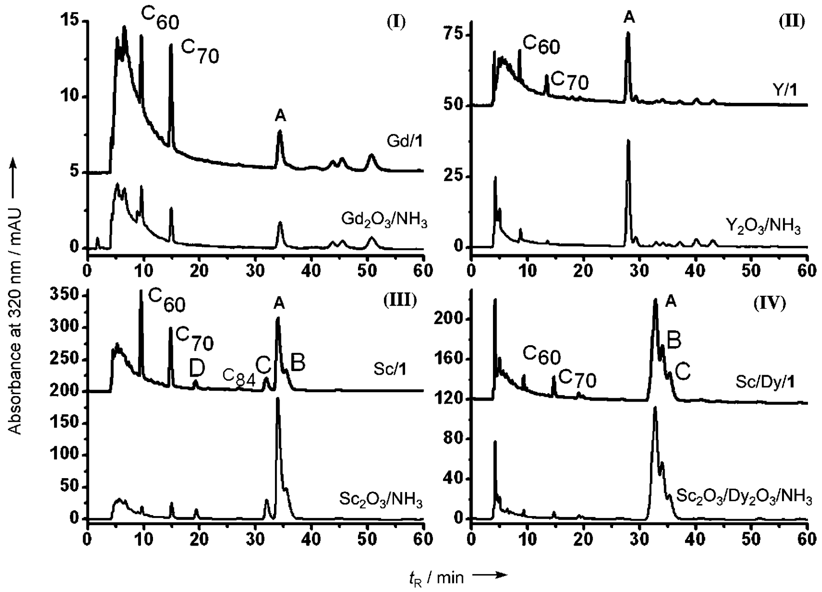


Figure 5. HPLC chromatograms of the M/**1** extracts in comparison with those obtained from the corresponding M_2O_3/NH_3 extracts (linear combination of two 4.6×250 mm Buckyprep columns; flow rate 1.6 mL min^{-1}; injection volume 100 μL; toluene as eluent (mobile phase); 40 °C). I) M = Gd, II) Y, III) Sc, and IV) Sc/Dy. Fraction A represents $Gd_3N@C_{80}$ (I, I_h), $Y_3N@C_{80}$ (I, I_h), $Sc_3N@C_{80}$ (I, I_h), and $Dy_xSc_{3-x}N@C_{80}$ (I, I_h, $x = 1, 2$) in I–IV, respectively. III) B, C, D represents $Sc_3N@C_{80}$ (II, D_{5h}), $Sc_3N@C_{78}$, and $Sc_3N@C_{68}$, respectively. IV) B, C represents $DySc_2N@C_{80}$ (I) + $DySc_2N@C_{76}$ + $Dy_xSc_{3-x}N@C_{80}$ (II, D_{5h}) (major), and $Sc_3N@C_{80}$ (I, I_h) (major), respectively.

Interpretation of the effect of the different nitrogen sources 1–5: The results of different nitrogen compounds **1**–**5** for the synthesis of NCFs are summarized in Scheme 2, which illustrates also the previously reported three methods: the "trimetallic nitride template" (TNT) process (IV),[5] the "inorganic solid nitrogen" route (II),[3] and the "reactive gas atmosphere" route (III).[2,3] For routes III and IV, the gaseous nitrogen atoms were used in a very different state with completely different effects on the selectivity of the resulting NCFs. Route II fulfils the high selectivity of NCFs like route III but has the disadvantage of the insufficient reproducibility of the fullerene yield, which might be caused by different levels of water impurities.[3] As a modification of route II, in this study we used a hydrogen-containing organic solid nitrogen. The guanidinium salts **1** and **2** achieved not only the comparable high selectivity of NCFs but also an improved

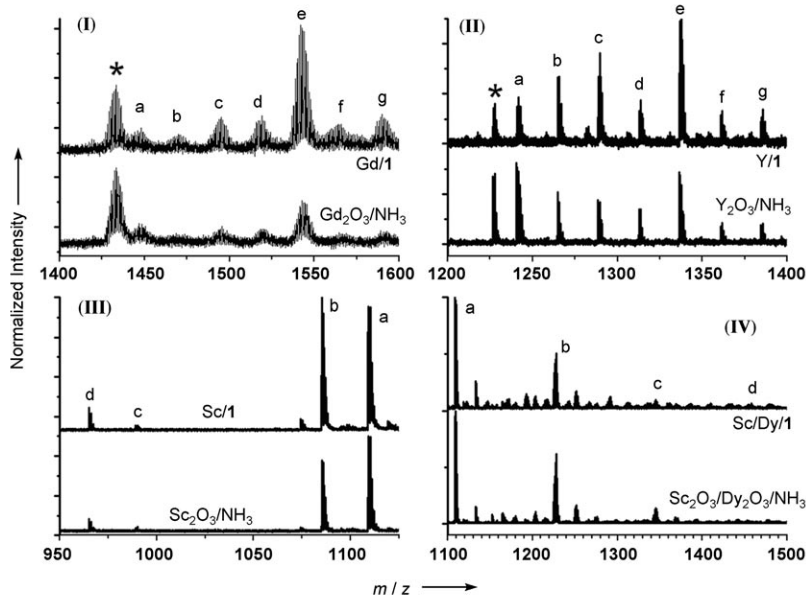


Figure 6. Enlarged LD-TOF MS of the M/**1** extract mixtures in comparison with those obtained from the corresponding M_2O_3/NH_3 extracts (positive-ion mode), emphasizing the major NCF products. I) M = Gd, II) Y, III) Sc, and IV) Sc/Dy. I and II) a–d represents $M_3N@C_{2n}$ (M = Gd, Y, $40 \leq n \leq 46$), respectively. The asterisks mark M_3C_{80}. III) a, b, c, d represents $Sc_3N@C_{80}$, $Sc_3N@C_{78}$, $Sc_3N@C_{70}$, and $Sc_3N@C_{68}$, respectively. IV) a, b, c, d represents $Sc_3N@C_{80}$, $DySc_2N@C_{80}$, $Dy_2ScN@C_{80}$, and $Dy_3N@C_{80}$, respectively.

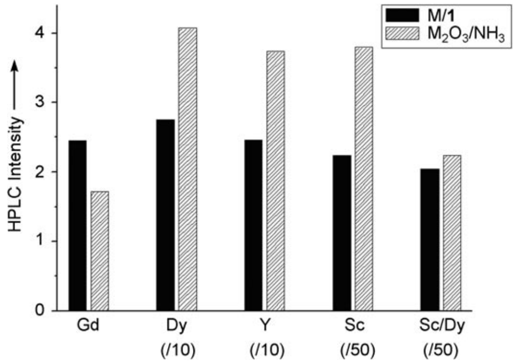
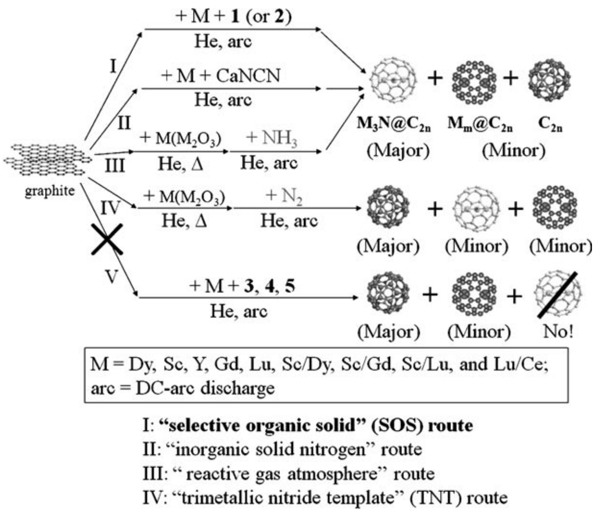


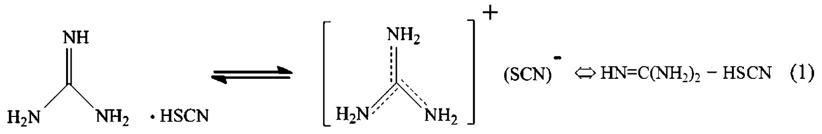
Figure 7. Comparison of the HPLC peak intensities of fraction A ($M_3N@C_{80}$ (I, I_h)) in Figure 1II and **5** obtained from the M/**1** and M_2O_3/NH_3 extracts, respectively. Note that for clarity the intensity for Dy, Y, Sc, and Sc/Dy is decreased 10, 10, 50, and 50 times, respectively.



Scheme 2. Schematic summary of different methods for the synthesis of NCFs by using different nitrogen sources including compounds **1**–**5** studied in the present work.

yield of NCFs like route III, whereas the attempt using organic solids **3**–**5** as nitrogen sources to synthesize NCFs (route V) failed. On the basis of such a distinct selectivity of the organic solids towards the formation of NCFs, we named route I the "selective organic solid" (SOS) route.

It is intriguing to understand why only the guanidinium salts **1** and **2** resulted in the successful formation of NCF, whereas the other three nitrogen sources **3**–**5** failed despite their structural similarity with **1** and **2** or NH_3. Given that compounds **1**–**5** are all small molecules and are easily decomposed under high-temperature conditions generated by the arc discharge, the different thermal decomposition properties of **1**–**5** are believed to be attributable to their dramatic differences in the formation of NCFs. Thermal decompositions of various guanidinium salts such as guanidinium nitrate under conventional heating conditions (<300 °C) have been extensively studied in the literature,[36,37] and accordingly the decompositions of **1** under arc-discharging conditions could be proposed as illustrated in Scheme 3. Although the guanidinium salt resonance structure is expected for **1** initially, under thermal conditions, **1** would be easily decomposed to guanidine



$$HN{=}C(NH_2)_2 \rightarrow N{\equiv}C(NH_2) + NH_3 \quad (2)$$

$$N{\equiv}C(NH_2) + M + C \rightarrow MN + (CN)_2 + H_2 \quad (3)$$

Scheme 3. Possible reaction schemes of **1**, metal (M), and graphite under arc-discharge conditions that lead to the formation of MN, which is reacted further to form $M_3N@C_{2n}$.[3]

($HN{=}C(NH_2)_2$) and HSCN (step 1 of Scheme 3).[36,37] This is strongly supported by the fact that both of two guanidinium salts **1** and **2** with different anions (SCN^- and Cl^-, respectively) result in a comparable yield of NCFs. The as-generated guanidine ($HN{=}C(NH_2)_2$) molecules are further decomposed under thermal conditions, thereby affording NH_3 and the intermediate $N{=}C(NH_2)$ molecules (step 2 of Scheme 3).[37] Clearly, the in situ generated NH_3 would result in the formation of NCFs following the reported reactive gas atmosphere route.[3] Furthermore, the highly reactive intermediate molecule $N{=}C(NH_2)$ would react readily with metal M and graphite, thus generating the nitride structure MN (step 3 of Scheme 3), which then follows the reaction mechanism proposed in ref. [3] to lead to the formation of the $[M_3N]^@$ intermediate. Clearly, the nitrogen atoms from both the in situ generated NH_3 and $N{=}C(NH_2)$ intermediate molecules contribute concurrently to the formation of NCFs.

Although **2** is expected to have a similar reaction mechanism for the synthesis of NCFs through step 1, in which **2** is decomposed to guanidine ($HN{=}C(NH_2)_2$) and HCl, the question of why nitrogen sources **3**–**5** failed to contribute in the formation of NCF and suppressed the formation of the endohedral metallofullerenes like $Dy@C_{82}$ is still open. The plausible explanation is that **3**–**5** could not generate in situ the NH_3 molecule and reactive $N{=}C(NH_2)$ molecules because of the differences in the chemical bonding of nitrogen and carbon atoms. Besides, although **4** has a comparable content of nitrogen atom to those in **1** and **2**, **4** is not a workable nitrogen source for the formation of NCF, thus suggesting that the content of nitrogen atoms in the molecule plays a minor role in the formation of NCF.

With respect to the inorganic nitrogen source **5**, although it is composed of NH_3 and HSCN, its performance in the formation of NCF as well as the empty fullerenes and endohedral metallofullerenes is completely different to NH_3, thereby suggesting that the $[NH_4]^+$ cation is not decomposed to NH_3 under arc-discharging condition. Therefore it does not contribute to the formation of NCF and has an adverse effect on the formation of the endohedral metallofullerenes. Compared to NH_3, the generation of the $[M_3N]^@$ intermediate as proposed in ref. [3] seems impossible with source **5**, consequently prohibiting the formation of NCF. Besides, it is also possible that the $[SCN]^-$ anion has a similar suppressing effect on both NCF and endohedral metallofullerenes. Interestingly, although there is $[SCN]^-$ anion in **1** as well, it has little effect on the formation of NCF because substituting SCN^- (in **1**) by Cl^- (in **2**) did not result in a clear change of the yield of NCF, thus suggesting that $[SCN]^-$ anion formed through the resonance structure of **1** and **2** might behave in a way that is quite different to the pure $[SCN]^-$ anion of **5** towards the formation of NCF. Interestingly, some papers reported the synthesis of guanidinium thiocyanate (**1**) using ammonium thiocyanate (**5**) as the reactant in solid state.[38] Our results suggest that, as the reverse procedure of those reported synthesis, **5** could not be formed upon the thermal decomposition of **1** (otherwise a similar effect of **5** to **1** would happen). This suggestion supports our proposed decomposition route of **1** under arc-discharging conditions as shown in step 1 of Scheme 3.

It should be noted that, in routes III and IV, before introducing the gaseous nitrogen for arc discharging, a heating pretreatment up to 1000 °C is generally necessary to "activate" the metal (or metal oxide) forming a carbide structure, thus requesting an additional heating furnace or an in-situ heating procedure.[1] In our developed selective organic solid (SOS) route, metal, guanidinium salts **1** and **2**, and graphite are simply mixed and subject to arc discharging directly without any additional heating pretreatment (see route I). Hence, the SOS route is clearly more facile than routes II and III.

Conclusion

In summary, we have developed a new "selective organic solid" (SOS) route for the facile synthesis of NCF by using two different guanidinium salts **1** and **2** as the new nitrogen sources. The optimum molar ratio of **1**/Dy/C has been determined to be 2.5:1:10. This new route has been successfully applied to the synthesis of NCFs based on metals M including Sc, Y, Gd, Dy, and Lu, and mixed metals Sc/Dy, Sc/Gd, Sc/Lu, and Lu/Ce, thus indicating that this is a general route toward the synthesis of NCFs. For several representative metals such as Sc, Y, Gd, Dy, and Sc/Dy, we quantitatively compared the yield of $M_3N@C_{80}$ synthesized by the SOS route with the reported reactive gas atmosphere route, thereby indicating that the yield of $M_3N@C_{80}$ by using **1** could be comparable to that obtained from the reactive gas atmosphere route in dependence on the metal.

Three other nitrogen sources (**3**–**5**) mixed with Dy metal were studied for comparison but did not result in the formation of Dy-NCF. To interpret the reason why only the guanidinium salts **1** and **2** resulted in the successful formation of NCF whereas the other three nitrogen sources **3**–**5** failed despite their structural similarity with **1** and **2** or NH_3, we propose the possible reaction schemes of **1**, metal, and graphite under arc-discharge conditions by analyzing the thermal decomposition of **1**. We conclude that the nitrogen atoms from both the in situ generated NH_3 and $N{=}C(NH_2)$ molecules contribute concurrently to the formation of NCFs.

In general, as a new and general route for the synthesis of NCFs, the SOS route developed in this work promises both the high selectivity of NCFs and the high reproducibility of fullerene yield. In addition, compared to the reported "trimetallic nitride template" (TNT) process and the "reactive gas atmosphere" route, no additional heating pretreatment is needed in the SOS route, thus simplifying the procedure and being more facile. With such advantages, we believe that the SOS route would open up a practicable way for enhancing the yield of NCFs based on some specific metals and expect that further nitrogen sources could be applied following this strategy.

Experimental Section

All nitrogen compounds studied in this work (guanidinium thiocyanate (**1**), guanidinium hydrochloride (**2**), 3,5-diamino-1,2,4-triazole (**3**), thiosemicarbazide (**4**), and ammonium thiocyanate (**5**)) were purchased from Aldrich and used as received.

The synthesis of fullerenes including NCFs was carried out by a modified Krätschmer–Huffman DC-arc-discharging method. Metals (Dy, Sc, Y, Gd, and Lu mixed metals Sc/Dy, Sc/Gd, Sc/Lu, and Lu/Ce, all are from MaTeck GmbH, Germany), the different nitrogen compounds **1**–**5**, and graphite powder were mixed in an optimum molar ratio of 2.5:1:15 (**1**:M:C) and filled into the drilled graphite rod, which was subjected to DC-arc discharging. In the experiment to optimize the synthesis conditions of Dy-NCFs by using **1**, the molar ratios of **1**/Dy ranged from 0.5:1 to 3:1 by varying the amount of **1** while the molar ratio of Dy/C is fixed at 1:10 according to the previous study. For synthesis of NCFs based on the mixed metals M1/M2 (Sc/Dy, Sc/Gd, Sc/Lu, and Lu/Ce), the optimized molar ratio of the 2.5:1:1(**1**/M1/M2) is used. The DC-arc discharging was carried out under 200 mbar He and an input current of 100 A. The synthesis by the "reactive gas atmosphere" route (using NH_3) was reported elsewhere.[2,3,7]

After DC-arc discharging, the soot was collected under ambient conditions, preextracted by acetone, and further Soxhlet-extracted by CS_2 for 20 h. The resulting solution was distilled to remove CS_2, and the mixture powder was immediately redissolved in toluene and subsequently passed through a 0.2 μm Telflon filter (Sartorius AG, Germany) for an HPLC test run, which was performed using a Hewlett–Packard instrument (series 1050), with toluene used as the eluent (mobile phase). A linear combination of two analytical 4.6×250 mm Buckyprep columns (Nacalai Tesque, Japan), a flow rate of 1.6 mL min^{-1}, and an injection volume of 100 μL were used. An UV detector set to 320 nm was used for fullerene detection. The LD-TOF MS analysis of the extract mixture was run in both positive and negative ion modes (Biflex III, Bruker, Germany).

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