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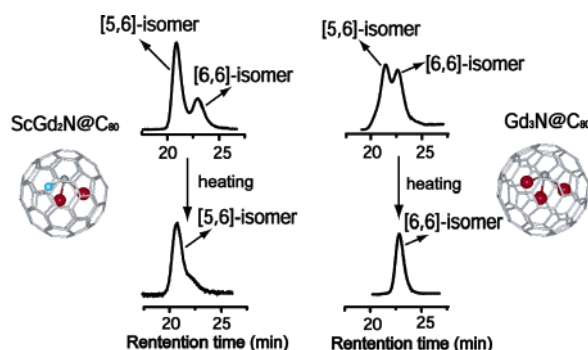
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ABSTRACT



We report a combined experimental and theoretical investigation on the regiochemistry of a series of TNT endohedral fullerenes $\text{Sc}_x\text{Gd}_{3-x}\text{N}@\text{C}_{80}$ ($x = 0-3$) in 1,3-dipolar cycloadditions, which demonstrates that the regioselectivity of the TNT-based endohedral fullerenes $\text{Sc}_x\text{Gd}_{3-x}\text{N}@\text{C}_{80}$ ($x = 0-3$) in the exohedral cycloadditions depends remarkably on the size of the encaged cluster.

Since the discovery of endohedral metallofullerene (EMF) $\text{La}@\text{C}_{60}$ in 1985,¹ a large number of EMFs have been synthesized and characterized over the past two decades.² However, little has been known about the exohedral chemistry of EMFs until very recently. The $\text{C}_{80}\text{-I}_h$ -based EMFs,

$\text{La}_2@\text{C}_{80}$ and $\text{M}_3\text{N}@\text{C}_{80}$ ($\text{M} = \text{Sc}, \text{Y}$), were recently found to be subject to exohedral [4+2] and 1,3-dipolar cycloadditions.^{3,4} It was observed that the 1,3-dipolar cycloaddition of azomethine ylide to $\text{M}_3\text{N}@\text{C}_{80}$ ($\text{M} = \text{Sc}, \text{Y}$) can occur at the [5,6]- and [6,6]-ring fusions of the $\text{C}_{80}\text{-I}_h$ cage, but the kinetically favored [6,6]-adduct can be quickly and completely transformed into the thermodynamically more stable [5,6]-adduct in the $\text{Sc}_3\text{N}@\text{C}_{80}$ case,^{4b} whereas such transformation is incomplete in the $\text{Y}_3\text{N}@\text{C}_{80}$ case.^{4a,5} This implies the size of the endohedral cluster subtly affects the regiochemistry of $\text{Sc}_3\text{N}@\text{C}_{80}$ and $\text{Y}_3\text{N}@\text{C}_{80}$, since these trimetallic

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nitride template (TNT) endohedral fullerenes share the same I_h -C₈₀ cage with similar electronic structures (M₃N)⁶⁺@C₈₀⁶⁻. Note that in addition to Sc₃N@C₈₀^{6a} and Y₃N@C₈₀, a number of TNT endohedral fullerenes M₃N@C₈₀ (M = lanthanide such as Gd, Dy, etc.)⁷ also have been synthesized and all of them have the similar valence state (M₃N)⁶⁺@C₈₀⁶⁻ but different sizes of the endohedral M₃N cluster. Among them, the Gd₃N@C₈₀ has the largest encaged cluster. If the regiochemistry of the TNT endohedral fullerenes depends largely on the size of the endohedral cluster, we wonder if the Gd₃N@C₈₀ would show thoroughly different regiochemistry from that of Sc₃N@C₈₀ and Y₃N@C₈₀ in the 1,3-dipolar cycloaddition. Herein we report a combined experimental and theoretical investigation on the regiochemistry of a series of TNT endohedral fullerenes Sc_xGd_{3-x}N@C₈₀ ($x = 0-3$) in 1,3-dipolar cycloadditions, which demonstrates that the [6,6]-pyrrolidino-adducts of Gd₃N@C₈₀ is the major product with minor [5,6]-pyrrolidino-adducts, a regioselectivity that is drastically different from that of Y₃N@C₈₀^{4a} and Sc_xGd_{3-x}N@C₈₀ ($x = 1-3$).

The endohedral fullerenes Sc_xGd_{3-x}N@C₈₀ ($x = 0-3$) were prepared and characterized following a similar process as previously reported.⁶ Isomerically pure samples of 10 mg of Sc₃N@C₈₀, 5 mg of Sc₂GdN@C₈₀, 5 mg of ScGd₂N@C₈₀, and 1 mg of Gd₃N@C₈₀ were isolated and dried in a vacuum. Next, ca. 0.5 mg of each sample was taken to dissolve in *o*-dichlorobenzene, and the solution was heated to 115 °C; afterward ¹³C-enriched formaldehyde and an excess of *N*-ethylglycine were added to react with the endohedral fullerenes under this temperature. After 15 min, the samples were cooled and HPLC with a Buckyprep-M column was applied to isolate the reacting products. The resulting HPLC profiles for the four samples are shown in Figure 1. Each

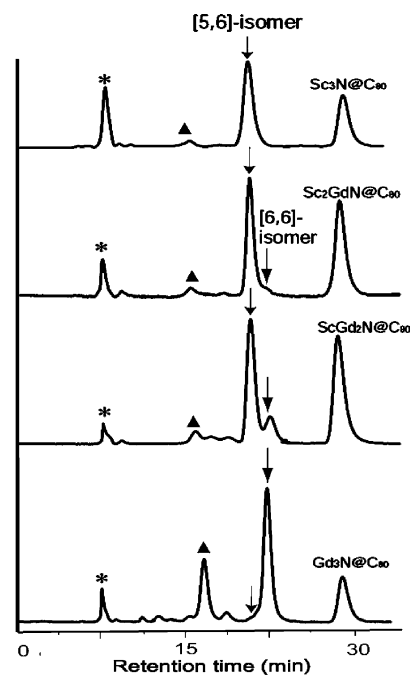


Figure 1. HPLC (Buckyprep-M, toluene eluent at 12 mL/min) profile of products of 1,3-dipolar cycloaddition of *N*-ethylazomethine ylide, in which pyrrolidinofullerenes [C₄H₉N]-Sc_xGd_{3-x}N@C₈₀ ($x = 0-3$) are the main products: (*) *o*-dichlorobenzene peak and (▲) bisadducts of Sc_xGd_{3-x}N@C₈₀ ($x = 0-3$) fullerenes.

fraction of the HPLC profiles was collected and analyzed by Matrix Assisted Laser Desorption/Ionization Mass Spectrometry (MALDI-MS) to determine the composition. The fractions with retention time at 19.6–23.9 min were assigned as the pyrrolidinofullerene monoadducts (Figure S1), and other fractions were *o*-dichlorobenzene, the unreacted Sc_xGd_{3-x}N@C₈₀ ($x = 0-3$), and pyrrolidinofullerene bisadducts, respectively (Figure 1).

The cycloaddition reactions of *N*-ethylazomethine ylide with Sc₃N@C₈₀ and Y₃N@C₈₀ under similar conditions have been studied previously.^{4b} It was revealed that the retention times of the pyrrolidinofullerenes on Buckyprep-M column depend exclusively on the [5,6]- or [6,6]-regioisomers, regardless of the different encaged M₃N clusters. This was ascribed to the fact that all the M₃N@C₈₀-I_h analogues have the same C₈₀-I_h cage and similar electronic structure.^{4a} Accordingly, the retention time can be used as a convenient tool to assign the regioisomers of the M₃N@C₈₀ analogues concerned herein.

As shown in Figure 1, a single peak (retention time 20.1 min) of the Sc₃N@C₈₀ monoadducts in the HPLC profile should represent the well-characterized [5,6]-[C₄H₉N]-Sc₃N@C₈₀.^{4b} Beginning with Sc₂GdN@C₈₀, a second peak appears after the [5,6]-regioisomer peak, which is shown as a peak tail in the HPLC profile of Sc₂GdN@C₈₀ derivatives,⁸ a minor peak in the HPLC profile of ScGd₂N@C₈₀ derivatives, and the major peak in the HPLC profile of Gd₃N@C₈₀ derivatives.⁹ MALDI-MS study reveals that the second peak has the same chemical composition as the first [5,6]-

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pyrrolidino-adduct peak. It was assigned as the [6,6]-pyrrolidino-adduct of $\text{Gd}_3\text{N}@\text{C}_{80}$, because its retention time (~ 22.7 min) is identical with the retention time (22.7 min) of the [6,6]-pyrrolidino- $\text{Y}_3\text{N}@\text{C}_{80}$ under the same HPLC condition. From Figure 1, it is clear that the [6,6]-product becomes more and more favored with the increasing TNT size from Sc_3N to Gd_3N , and the [6,6]-product finally became the major regioisomer in the Gd_3N case.

To further explore the relative thermostability of the [6,6]- and [5,6]-regioisomers, we then performed a thermal treatment of the reacting products at 180 °C for 1 h in combination with HPLC analyses. The results showed the following: (a) the major [5,6]-regioisomer of pyrrolidino- $\text{Sc}_3\text{N}@\text{C}_{80}$ is unchanged after thermalization as previously reported,^{4b} (b) the minor [6,6]-regioisomer of the $\text{Sc}_2\text{-GdN}@\text{C}_{80}$ derivative is completely isomerized to [5,6]-regioisomer; (c) the minor [6,6]-regioisomer of the $\text{ScGd}_2\text{N}@\text{C}_{80}$ derivative is partially isomerized to the [5,6]-regioisomer (Figure 2a,b), suggesting that in this case the energy

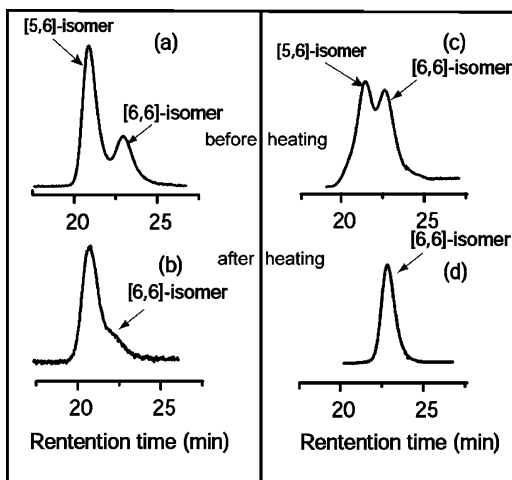


Figure 2. HPLC (Buckyprep-M, toluene eluent at 12 mL/min) profiles of reaction products: (a) $[\text{C}_4\text{H}_9\text{N}]\text{-ScGd}_2\text{N}@\text{C}_{80}$, (b) $[\text{C}_4\text{H}_9\text{N}]\text{-ScGd}_2\text{N}@\text{C}_{80}$ after 1 h of heating at 180 °C, (c) $[\text{C}_4\text{H}_9\text{N}]\text{-Gd}_3\text{N}@\text{C}_{80}$, and (d) $[\text{C}_4\text{H}_9\text{N}]\text{-Gd}_3\text{N}@\text{C}_{80}$ after 1 h of heating at 180 °C.

difference between [5,6]- and [6,6]-isomers is very small; and (d) the major [6,6]-pyrrolidino- $\text{Gd}_3\text{N}@\text{C}_{80}$ is unchanged, whereas the minor [5,6]-adducts (enriched sample, Figure 2c,d) is isomerized to [6,6]-adducts, indicating that [6,6]-adducts are both kinetically and thermodynamically favored in this case.

(8) We collected the pyrrolidinofullerene fractions of $\text{Sc}_3\text{N}@\text{C}_{80}$ and $\text{Sc}_2\text{-GdN}@\text{C}_{80}$ with retention times at 21.4–24.0 min and performed the HPLC again. It can be seen that the former maintains a single peak while the latter sample shows two distinct peaks (Figure S2, Supporting Information) in the HPLC profiles.

(9) The pyrrolidinofullerene fractions of $\text{Gd}_3\text{N}@\text{C}_{80}$ with retention times at 21.4–24.0 min are collected and HPLC was performed again. It shows a minor peak with short retention time appears before the major peak, which was assigned as the [5,6]- $\text{Gd}_3\text{N}@\text{pyrrolidino-C}_{80}$ regioisomer.

To understand the observed different regioselectivities of $\text{Sc}_x\text{Gd}_{3-x}\text{N}@\text{C}_{80}$ ($x = 0-3$), all-electron relativistic density functional calculations at the PBE/DNP level of theory¹⁰ were performed to evaluate the relative energy of all [5,6]- and [6,6]-regioisomers. As shown in Table 1, the energetic

Table 1. PBE/DNP-Predicted Key Geometric Parameters (Bond Length, in Å; Angle in deg) of $\text{Sc}_x\text{Gd}_{3-x}\text{N}@\text{C}_{80}$ ($x = 0-3$) and Formation Energies (RE, in kcal/mol) of and Energy Differences (ΔE , in kcal/mol) between the [6,6]- and [5,6]-Regioisomers of Pyrrolidinofullerenes

	$\text{Sc}_3\text{N}@\text{C}_{80}$	$\text{Sc}_2\text{GdN}@\text{C}_{80}$	$\text{ScGd}_2\text{N}@\text{C}_{80}$	$\text{Gd}_3\text{N}@\text{C}_{80}$
Sc–N	2.03	1.95	1.90	
Gd–N		2.18	2.11	2.12
Sc–C ^a	2.26	2.22	2.21	
Gd–C ^a		2.46	2.44	2.43
RE				
[6,6]-adduct	–34.1	–38.2	–43.8	–46.2
[5,6]-adduct	–45.8	–46.9	–46.1	–45.8
ΔE^b	11.7	8.7	2.3	–0.4

^a The nearest M to C (cage) distance. ^b $\Delta E = E_{\text{tot}}([\text{6,6}]\text{-adduct}) - E_{\text{tot}}([\text{5,6}]\text{-adduct})$.

difference (ΔE) between [5,6]- and [6,6]-adducts is quite large (11.7 kcal/mol) for $\text{Sc}_3\text{N}@\text{C}_{80}$. Along with the encaged M_3N cluster size increasing from Sc_3N to Gd_3N , ΔE decreases to 8.7 kcal/mol for $\text{Sc}_2\text{GdN}@\text{C}_{80}$, 2.3 kcal/mol for $\text{ScGd}_2\text{N}@\text{C}_{80}$, and -0.4 kcal/mol for $\text{Gd}_3\text{N}@\text{C}_{80}$. Clearly, due to the very large size of Gd_3N , an inversed regioselectivity is expected for the pyrrolidino-adducts of $\text{Gd}_3\text{N}@\text{C}_{80}$, which is well in line with the experimental results.

In summary, our combined experimental and theoretical investigation clearly demonstrates that the regioselectivity of the TNT-based endohedral fullerenes $\text{Sc}_x\text{Gd}_{3-x}\text{N}@\text{C}_{80}$ ($x = 0-3$) in the exohedral cycloadditions depends remarkably on the size of the encaged cluster, i.e., [5,6]-regioisomers being major products in the $\text{Sc}_x\text{Gd}_{3-x}\text{N}@\text{C}_{80}$ ($x = 1-3$) cases and [6,6]-regioisomers being major products for the largest $\text{Gd}_3\text{N}@\text{C}_{80}$.

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Supporting Information Available: Details of experiments and computed structures of the pyrrolidinofullerenes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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