Size Effect of Encaged Clusters on the Exohedral Chemistry of Endohedral Fullerenes: A Case Study on the Pyrrolidino Reaction of $\text{Sc}_x\text{Gd}_{3-x}\text{N@C}_{80}$ ($x=0-3$)

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S1. The synthesis and HPLC separation of $\text{Sc}_x\text{Gd}_{3-x}\text{N@C}_{80}$ ($x=0-3$)

Mixture of Sc/Ni alloy, Gd/Ni alloy and graphite powder were pressed into the holes of graphite-rod electrodes in a molar Sc:Gd:C ratio of 1:1:24. As the resource of nitrogen, 3Torr N_2 was introduced to reactor at the atmosphere of 300 Torr He. The fullerene soot generated was Soxlet-extracted with toluene and purified by HPLC. Multi-stage HPLC technique is employed to isolate and purify the endohedral fullerenes, using two complementary columns: Cosmosil Buckyprep, and Cosmosil Buckyprep-M.

$\text{Sc}_3\text{N@C}_{80}$ were isolated from the soot extract (Sc/C composite rods in arc-discharge) and purified via a two-stage of high-performance liquid chromatography (HPLC). Buckyprep column separates fullerenes according to their size. In the first stage, the Buckyprep column was used to collect the $\text{C}_{88}\text{-C}_{90}$ fraction. Buckyprep-M separates fullerenes according to their polarity (similar to Buckyclutcher column), which was employed in the second stage to remove the hollow fullerenes (C_{88} , C_{90}) from $\text{Sc}_3\text{N@C}_{80}$. The stage 1 and 2 were repeated several times until pure $\text{Sc}_3\text{N@C}_{80}$ being collected. $\text{Gd}_3\text{N@C}_{80}$ was separated via a similar process (soot extract from Gd/C composite rods arc-discharge) as $\text{Sc}_3\text{N@C}_{80}$, only the collection fractions are different for them due to the different retention times of $\text{Sc}_3\text{N@C}_{80}$ and $\text{Gd}_3\text{N@C}_{80}$.

$\text{Sc}_2\text{GdN@C}_{80}$ and $\text{ScGd}_2\text{N@C}_{80}$ were isolated from the soot extract (Sc/Gd/C composite rods arc-discharge) and purified via a four-stage HPLC process. The first stage used the Buckyprep column to collect the $\text{C}_{88}\text{-C}_{90}$ fraction, the second stage is performed in a Buckyprep-M column to remove the hollow fullerenes. The third stage of HPLC utilized Buckyprep column again but recycling function is employed to separate $\text{Sc}_3\text{N@C}_{80}$, $\text{Gd}_3\text{N@C}_{80}$,

$\text{Sc}_2\text{GdN@C}_{80}$, $\text{ScGd}_2\text{N@C}_{80}$ into four different fractions. The fourth stage HPLC used the Buckyprep column in recycling mode to purify the isolated $\text{Sc}_2\text{GdN@C}_{80}$ and $\text{ScGd}_2\text{N@C}_{80}$.

Figure S1. MALDI-MS of the monoadducts of pyrrolidinofullerenes. a) $\text{Sc}_3\text{N@C}_{80}$, b) $\text{Sc}_2\text{GdN@C}_{80}$, c) $\text{ScGd}_2\text{N@C}_{80}$ and d) $\text{Gd}_3\text{N@C}_{80}$. $\text{Sc}_3\text{N@C}_{80}$, $\text{Sc}_2\text{GdN@C}_{80}$, $\text{ScGd}_2\text{N@C}_{80}$ and $\text{Gd}_3\text{N@C}_{80}$ are fragments of the parent pyrrolidinofullerenes under laser desorption.

Figure S2. Comparative study of the HPLC (Buckyprep-M, toluene, 12ml/min) profiles of [5,6]-pyrrolidino- $\text{Sc}_3\text{N@C}_{80}$ and [5,6]/[6,6]-pyrrolidino- $\text{Sc}_2\text{GdN@C}_{80}$

Figure S3 PBE/DNP-predicted geometries of $\text{Sc}_x\text{Gd}_{3-x}\text{N@C}_{80}$ ($x=0-3$) and the [6,6]- and [5,6]-regioisomers of their pyrrolidino-adducts.