

## Electronic Supplementary Information for:

### Large mixed metal nitride clusters encapsulated in a small cage: The confinement of the C<sub>68</sub>-based clusterfullerenes

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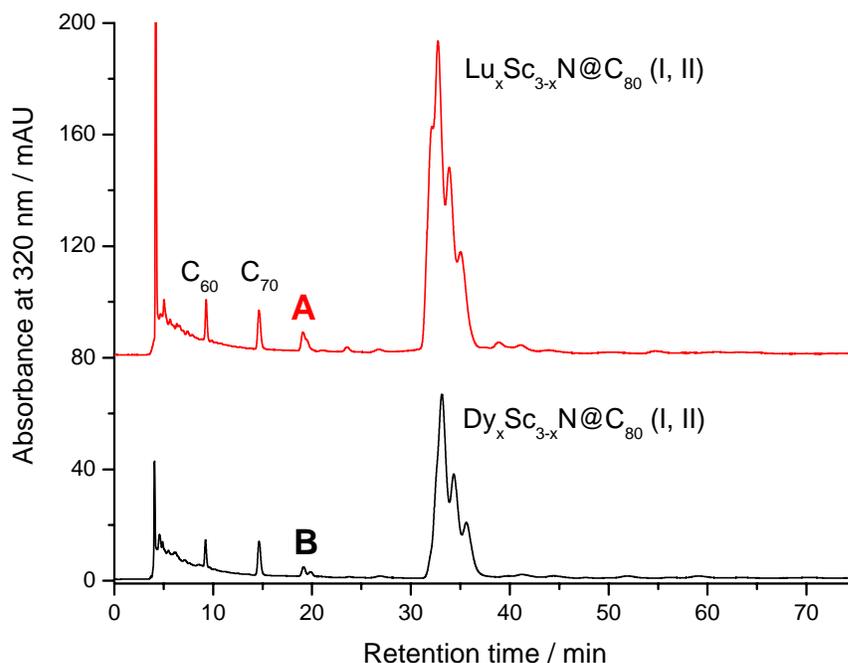
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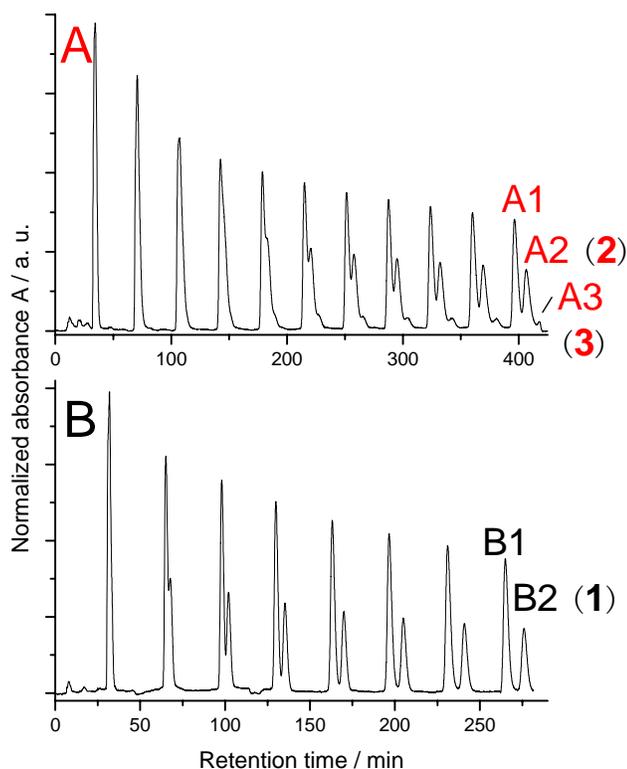
#### ***S1. Synthesis and isolation of DySc<sub>2</sub>N@C<sub>68</sub> (1), LuSc<sub>2</sub>N@C<sub>68</sub> (2) and Lu<sub>2</sub>ScN@C<sub>68</sub> (3):***

The three new nitride clusterfullerenes (NCFs) **1-3** are produced by a modified Krätschmer-Huffman DC-arc discharging method with the addition of NH<sub>3</sub> (20 mbar) as described before.<sup>1,9,10,13,15</sup> Briefly, a mixture of Dy<sub>2</sub>O<sub>3</sub> (Lu<sub>2</sub>O<sub>3</sub>) and Sc<sub>2</sub>O<sub>3</sub> (99.9%, MaTeck GmbH, Germany) and graphite powder was used (molar ratio of Dy:Sc:C(or Lu:Sc:C)=1:1:15). After DC-arc discharging, the soot was pre-extracted by acetone and further Soxhlet-extracted by CS<sub>2</sub> for 20 h. The extracted fullerene mixture is distilled and dissolved in toluene. Fullerene isolation was performed by two-step HPLC. In the first step running in a Hewlett-Packard instrument (series 1050), a linear combination of two analytical 4.6 × 250 mm Buckyprep columns (Nacalai Tesque, Japan) was applied with toluene as the eluent. The second-step isolation is performed by recycling HPLC (Sunchrom, Germany) using a semi-preparative Buckyprep column (Nacalai Tesque, Japan) and toluene as the eluent. A UV detector set to 320 nm was used for fullerene detection for both steps.



**Fig. S1.** The first-step HPLC isolations of the  $\text{Lu}_x\text{Sc}_{3-x}\text{N}@C_{2n}$  and  $\text{Dy}_x\text{Sc}_{3-x}\text{N}@C_{2n}$  fullerene extract mixtures synthesized by the “reactive gas atmosphere” method (combination of two 4.6 x 250 mm Buckyprep columns; flow rate 1.6 ml/min; injection volume 100  $\mu\text{l}$ ; toluene as eluent (mobile phase); 40°C). The dominant peaks with the retention of 30-37 min are the major products  $\text{M}_x\text{Sc}_{3-x}\text{N}@C_{80}$  (I, II) (M= Lu, Dy, x=0-3).

The typical chromatograms of a  $\text{Lu}_x\text{Sc}_{3-x}\text{N}@C_{2n}$  and  $\text{Dy}_x\text{Sc}_{3-x}\text{N}@C_{2n}$  fullerene extract mixtures obtained on two Buckyprep columns are shown in Fig. S1. Together with mass-spectroscopic (MS) analysis it shows that  $\text{Dy}_x\text{Sc}_{3-x}\text{N}@C_{2n}$  (a) and  $\text{Lu}_x\text{Sc}_{3-x}\text{N}@C_{2n}$  (b) NCFs (fractions A-D) (retention time 30 - 70 min) are the dominant products. This first step in HPLC results in isolation of fractions **A** and **B**, respectively, which are subject to the second-step isolation by recycling HPLC (Buckyprep column) and the corresponding chromatograms are illustrated in Fig. S2.



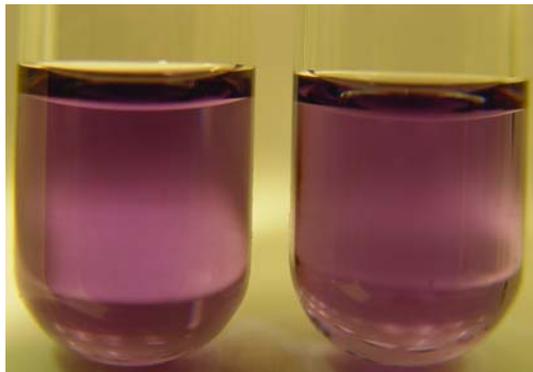
**Fig. S2.** The chromatograms of the isolated fractions **A** and **B** by the second-step recycling HPLC (10 x 250 mm Buckyrep-M column; flow rate 5.0 ml/min; injection volume 5 ml; toluene as eluent; 20°C). A1 and B1:  $\text{Sc}_3\text{N}@\text{C}_{68}$ , A2:  $\text{LuSc}_2\text{N}@\text{C}_{68}$  (**2**), A3:  $\text{Lu}_2\text{ScN}@\text{C}_{68}$  (**3**), B2:  $\text{DySc}_2\text{N}@\text{C}_{68}$  (**1**).

Based on the integrated HPLC peak area, the relative yield of **1** (**2**) to  $\text{Sc}_3\text{N}@\text{C}_{68}$  is estimated to be 1:2, while that of **3** to  $\text{Sc}_3\text{N}@\text{C}_{68}$  is ca. 1:12 (i.e., the relative yield of **3:2:Sc<sub>3</sub>N@C<sub>68</sub>** = 1:6:12) (see Fig. S2).

Besides, for  $\text{Lu}_x\text{Sc}_{3-x}\text{N}@\text{C}_{68}$  (fraction A), there are 3 isolable structures ( $x=0-2$ ). However, for  $\text{Dy}_x\text{Sc}_{3-x}\text{N}@\text{C}_{68}$  (fraction B), only  $\text{Sc}_3\text{N}@\text{C}_{68}$  and  $\text{DySc}_2\text{N}@\text{C}_{68}$  (**1**) formed. This indicates clearly the difference between Lu/Sc and Dy/Sc mixed NCFs.

***S2. Comparison of the colors of 1-3 and Sc<sub>3</sub>N@C<sub>68</sub> solutions (in toluene):***

Owing to the same cage symmetries ( $D_3:6140$ ) of **1-3** and Sc<sub>3</sub>N@C<sub>68</sub>, the electronic absorption properties of **1-3** are almost identical to that of Sc<sub>3</sub>N@C<sub>68</sub> (see Fig. 2), as a result the colors of **1-3** dissolved in toluene are same to that of Sc<sub>3</sub>N@C<sub>68</sub> (purple) as clearly shown in Fig. S3.



**Fig. S3.** Photographs of Sc<sub>3</sub>N@C<sub>68</sub> (left) and DySc<sub>2</sub>N@C<sub>68</sub> (**1**) (right) dissolved in toluene. The colors of LuSc<sub>2</sub>N@C<sub>68</sub> (**2**) and Lu<sub>2</sub>ScN@C<sub>68</sub> (**3**) are same to **1**.