

Supporting Information

Tuneable Dynamics of Scandium Nitride Cluster Inside an I_h -C₈₀ Cage

Yongqiang Feng,^a Taishan Wang,^{*a} Junfeng Xiang,^a Lihua Gan,^b Bo Wu,^a Li Jiang,^a and Chunru Wang^{*a}

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Figure S2. HPLC profile and MALDI-TOF mass spectra of the purified Sc₃N@I_h-C₈₀ fulleropyrrolidine product (HPLC condition: 20×250 mm Buckyrep column; flow rate 12 mL/min; toluene as eluent).

Figure S3. HPLC profile of the Sc₃N@I_h-C₈₀-PCBM product mixture from the reaction. (HPLC condition: 20×250 mm Buckyrep-M column; flow rate 12 mL/min; toluene as eluent).

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Figure S6. MALDI-TOF mass spectra of the purified Sc_{3-x}Y_xN@I_h-C₈₀ (x = 0-3).

Figure S7. (a) ¹³C NMR (150 MHz) and (b) ⁴⁵Sc NMR (145 MHz) spectra of Sc₃N@I_h-C₈₀ in d₄-ODCB.

1. Synthesis and purification of $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$ fulleropyrrolidine

Prato reaction adduct of $\text{Sc}_3\text{N}@C_{80}$ was performed by mixing a solution of $\text{Sc}_3\text{N}@C_{80}$ with an excess of *N*-ethylglycine and paraformaldehyde in *o*-dichlorobenzene (ODCB) and stirred at 120 °C for 30 min. The product was isolated and purified by HPLC.

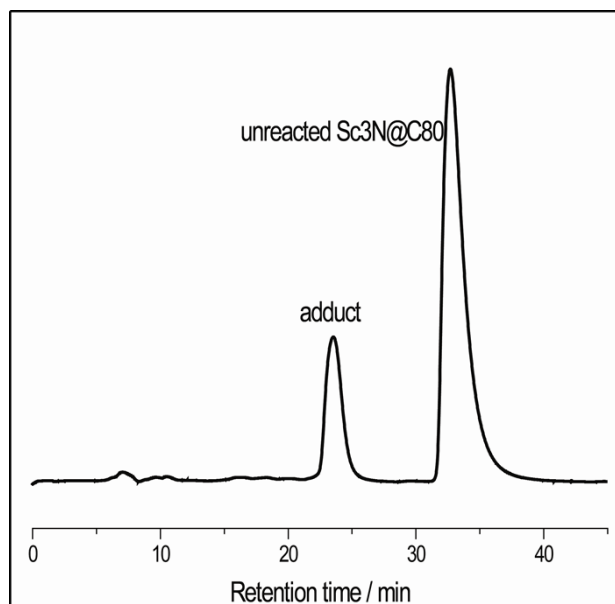


Figure S1. HPLC profile of the $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$ fulleropyrrolidine product mixture from the reaction. (HPLC condition: 20×250 mm Buckyprep-M column; flow rate 12 mL/min; toluene as eluent).

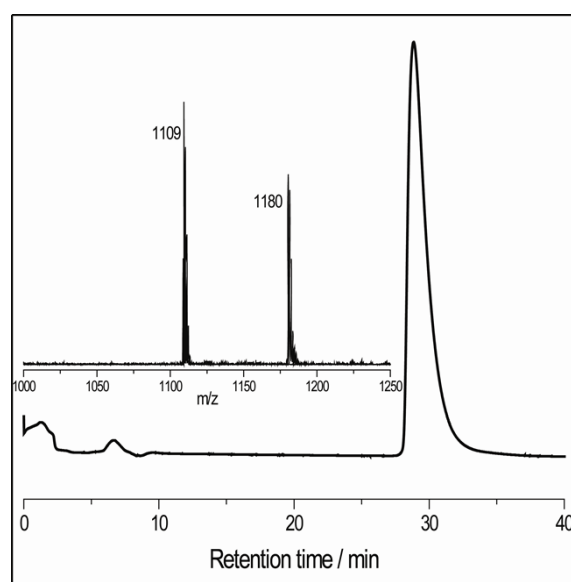


Figure S2. HPLC profile and MALDI-TOF mass spectra of the purified $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$ fulleropyrrolidine product (HPLC condition: 20×250 mm Buckyprep column; flow rate 12 mL/min; toluene as eluent).

2. Synthesis and purification of Sc₃N@C₈₀-PCBM

Sc₃N@C₈₀-PCBM (PCBM = phenyl-C₈₁-butyric acid methyl ester) was synthesized as reported previously.¹ To be brief, 56.1 mg of methyl 4-benzoylbutyrate p-tosylhydrazone was dissolved in 6 mL of pyridine in a dried three-necked flask provided with an Ar inlet and a magnetic stirring bar. Then, 8.4 mg of NaOMe was added, and the mixture was stirred for 15 min. A solution of 16.5 mg of Sc₃N@C₈₀ in 18 mL of HPLC grade 1,2-dichlorobenzene was added, and the homogeneous reaction solution was stirred at 70 °C for 24 h. The target Sc₃N@C₈₀-PCBM was isolated from the reaction mixture by HPLC.

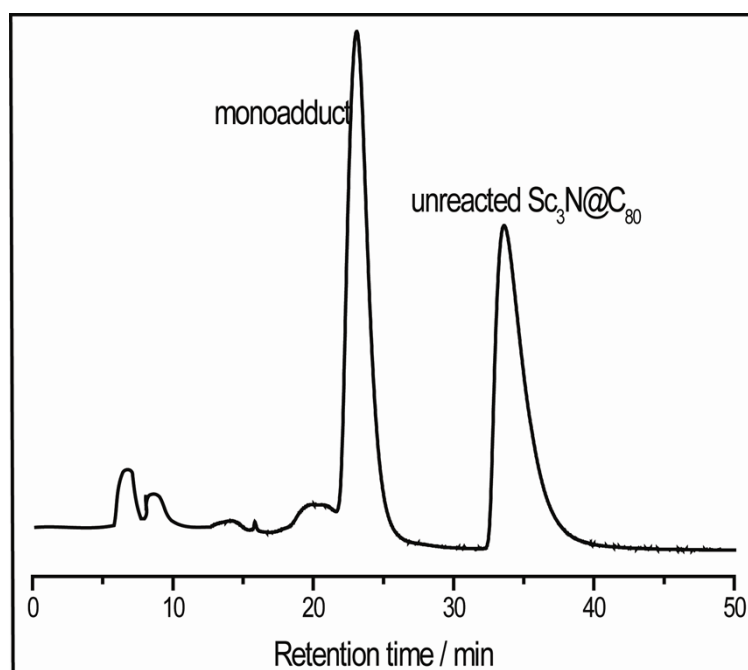


Figure S3. HPLC profile of the Sc₃N@I_n-C₈₀-PCBM product mixture from the reaction. (HPLC condition: 20×250 mm Buckyprep-M column; flow rate 12 mL/min; toluene as eluent).

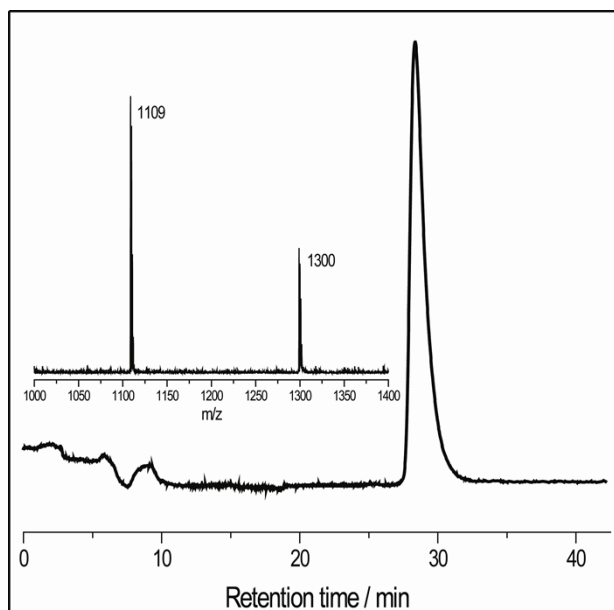


Figure S4. HPLC profile and MALDI-TOF mass spectra of the purified $\text{Sc}_3\text{N}@I_h\text{-C}_{80}\text{-PCBM}$ product (HPLC condition: 20×250 mm Buckyprep column; flow rate 12 mL/min; toluene as eluent).

3. The synthesis and purification of $\text{Sc}_{3-x}\text{Y}_x\text{N}@I_h\text{-C}_{80}$ ($x = 0-3$)

The scandium nitride clusterfullerenes $\text{Sc}_{3-x}\text{Y}_x\text{N}@I_h\text{-C}_{80}$ ($x = 0-3$) were synthesized by the Krätschmer-Huffman arc discharge method and isolated by the multistage high-performance liquid chromatography (HPLC) strategy.² Briefly, the mixture of Sc/Ni alloy, Y/Ni alloy and graphite powder with a mass ratio of 3: 3: 1 was packed into the core-drilled graphite rods, subsequently the rods were burnt at 120 A direct current under a total of 200 Torr atmosphere (97.5% He/2.5% N_2). The as-prepared soot was Soxhlet-extracted by toluene for 20 h, and the target molecules were isolated and purified by two complementary HPLC columns, that is, Buckyprep and Buckyprep-M. The high purity of each $\text{Sc}_{3-x}\text{Y}_x\text{N}@I_h\text{-C}_{80}$ ($x = 0-3$) sample was confirmed by a single-peak HPLC profile and a single-peak MALDI-TOF profile of corresponding counterpart

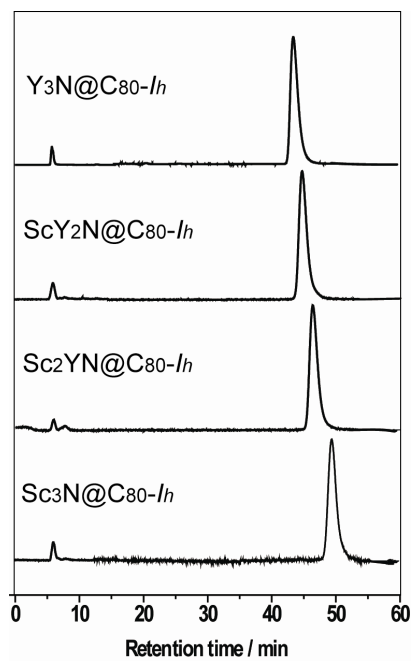


Figure S5. HPLC profile of the purified $\text{Sc}_{3-x}\text{Y}_x\text{N}@I_h\text{-C}_{80}$ ($x = 0-3$). (HPLC condition: 20×250 mm Buckyprep column; flow rate 12 mL/min; toluene as eluent).

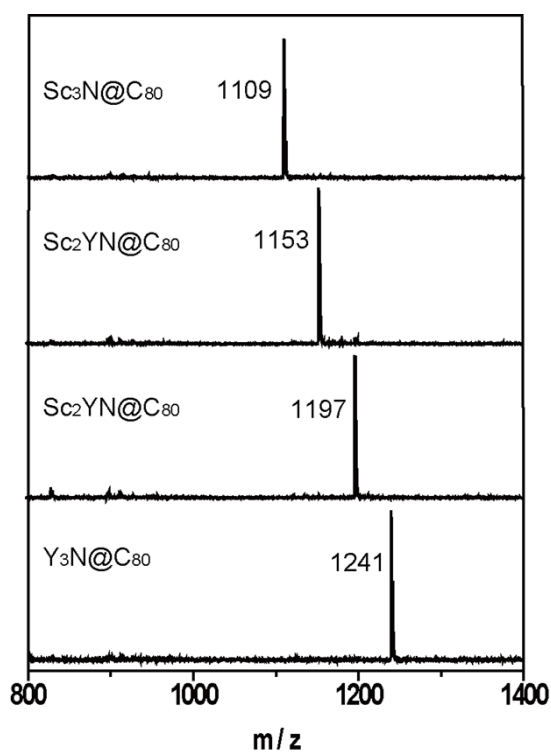


Figure S6. MALDI-TOF mass spectra of the purified $\text{Sc}_{3-x}\text{Y}_x\text{N}@I_h\text{-C}_{80}$ ($x = 0-3$).

4. ^{13}C NMR and ^{45}Sc NMR experiment

^{13}C NMR and ^{45}Sc NMR spectra were measured at 600 MHz on a Bruker AVANCE-600 spectrometer. For varied-temperature ^{45}Sc NMR measurement, CS_2 acted as the solvent and d_8 -THF as internal lock agent. For ambient-temperature ^{13}C and ^{45}Sc NMR measurement, *o*-dichlorobenzene- d_4 was chosen as solvent and internal lock agent.

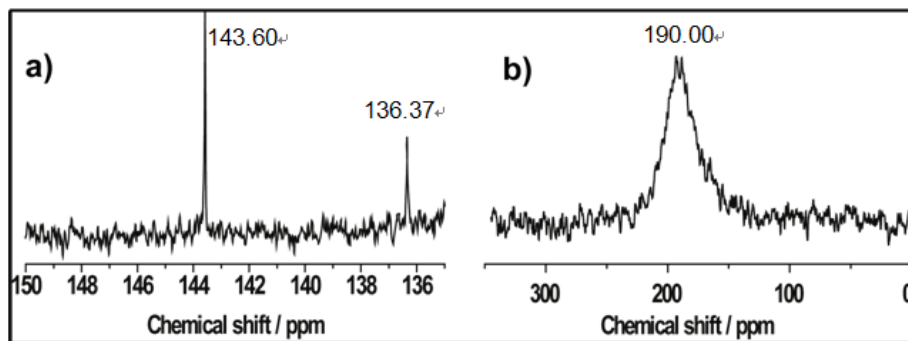


Figure S7. (a) ^{13}C NMR (150 MHz) and (b) ^{45}Sc NMR (145 MHz) spectra of $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$ in d_4 -ODCB.

5. DFT calculations

All the density functional theory (DFT) computations were performed by the generalized gradient approximation (GGA) functional of Perdew, Burke, and Ernzerhof /double numerical plus polarization using the DMol³ code in Accelrys Materials Studio.^{3,4}

References

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- 4 (a) B. Delley, *J. Chem. Phys.* **1990**, *92*, 508-517; (b) B. Delley, *J. Chem. Phys.* **2000**, *113*, 7756. DMol3 is available as part of Material Studio.