Electronic Supplementary Material (ESI) for Nanoscale
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Supporting Information

Size Effect of Endohedral Cluster on Fullerene Cage: Preparation and Structural Studies of $Y_3N@C_{78}$-C_2

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Experimental Section:

1. The synthesis and purification of $Y_3N@C_{78}$

Graphite rods were core-drilled and subsequently packed with a mixture of Y/Ni_2 alloy and graphite powder in a weight ratio of 2:1. These rods were then vaporized in a Krätschmer-Huffman generator at 192 Torr He and 8 Torr N_2. The resulting soot was Soxlet-extracted with toluene for 12 h. $Y_3N@C_{78}$ was isolated from various empty fullerenes and other yttrium metallofullerenes by multi-stage HPLC.

2. HPLC data of purified $Y_3N@C_{78}$

The stage 1 and 2 separations were repeated several times to obtain purified $Y_3N@C_{78}$. Figure S3 and Figure S4 show the HPLC data of purified $Y_3N@C_{78}$ with Buckyprep and Buckyprep-M columns. These HPLC analyses also confirm the purity of $Y_3N@C_{78}$.

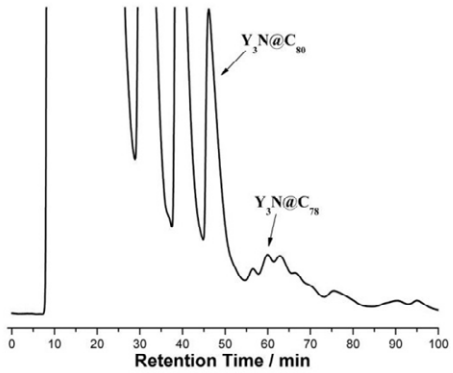

Figure S1. The first stage HPLC profile of toluene extract of the soot containing mostly yttrium endohedral metallofullerenes (20×250 mm Buckyprep column; flow rate 12 mL/min; toluene as eluent).

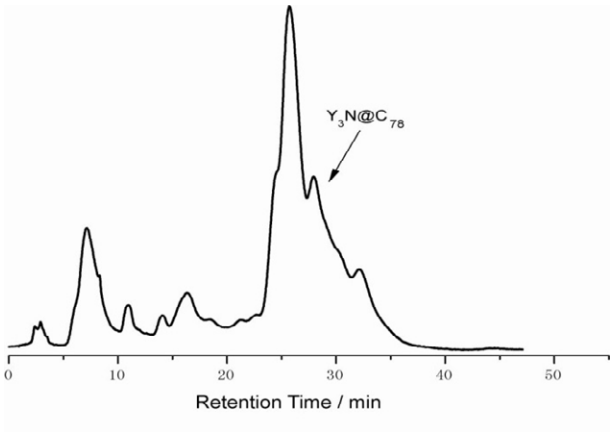

Figure S2. The second stage HPLC profile of $Y_3N@C_{78}$ fullerenes (20×250 mm Buckyprep-M column; flow rate 12 mL/min; toluene as eluent).

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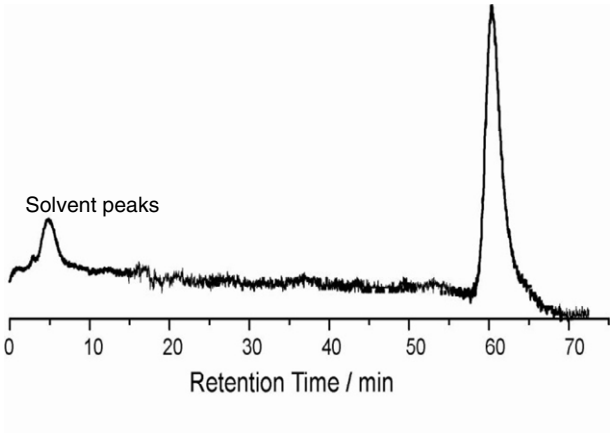

Figure S3. Chromatogram of the isolated $Y_3N@C_{78}$ (20×250 mm Buckyprep column; flow rate 12 mL/min; toluene as eluent).

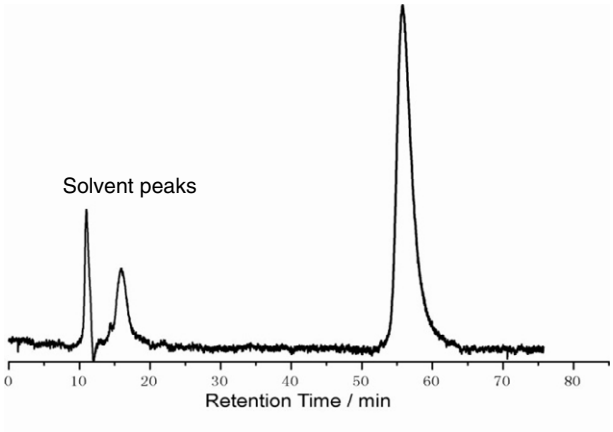

Figure S4. Chromatogram of the isolated $Y_3N@C_{78}$ (20×250 mm Buckyprep-M column; flow rate 6 mL/min; toluene as eluent).

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3. CV spectrum of purified $Y_3N@C_{78}$

Electrochemistry experiments were carried out in *o*-DCB solvent with glassy carbon as the working, Pt flake and a SCE as the counter and reference electrodes, respectively. The potentials were referred to the E value of the Fc/Fc^+ redox couple measured in the sample solution.

The first and second oxidation potentials, ${}_{ox}E_1$ and ${}_{ox}E_2$, appear at 0.25 V and 0.53 V, respectively. While the first and second reduction potentials, ${}_{red}E_1$ and ${}_{red}E_2$, appear at -1.62 V and -1.99 V, respectively.

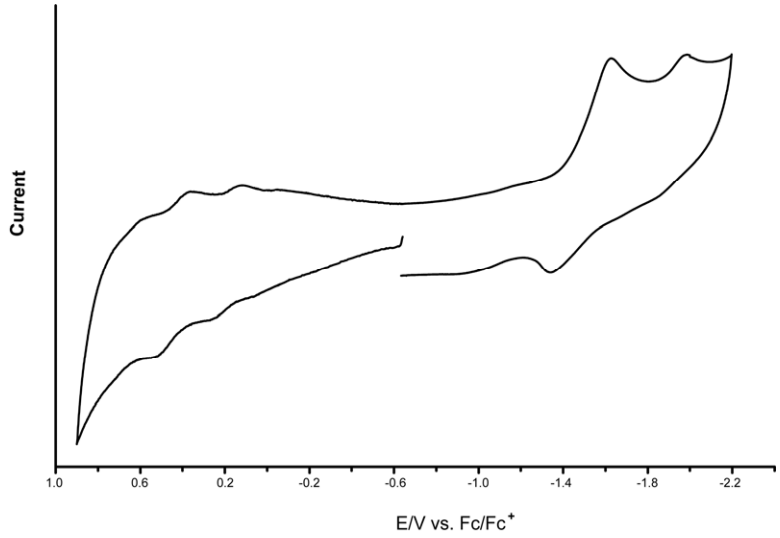

Figure S5. *CV spectrum of $Y_3N@C_{78}$ in o-DCB. 0.05 M $(n\text{-}Bu)_4NPF_6$; scan rate, 100 mV s^{-1}.*

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Calculation Section:

1. DFT calculated results of $Sc_xY_{3-x}N@C_{78}$ (x=0-3*)* isomers

Density functional theory (DFT) calculations were preformed to study the relative energies and geometric structures of $Sc_xY_{3-x}N@C_{78}$ (x=0-3*)* isomers at GGA-PBE/DNP[S1] level by using the Dmol^3 code[S2]. C_{78} has in total 24 109 isomers, and five of them conform with the IPR[S3]. As showed in reference S4, the IPR isomer D_{3h}: 24109, was found to be the most stable isomer of C_{78}^{6-}. The second most stable isomer is the non-IPR C_2: 22010 cage, which contains two pairs of adjacent pentagons.[S4] Therefore, we executed our calculations based on these two C_{78} isomers. The geometry optimizations were carried out with no symmetry and spin constraints in Cartesian coordinates and with analytically constructed energy gradient.

Table S1. Relative Energies (ΔE, kJ/mol) of $Sc_2YN@C_{78}$ isomers

Species	Δ*E*
$Sc_2YN@C_{78}$-D_{3h}	0
$Sc_2YN@C_{78}$-C_2	5.798376
$Sc_2YN@C_{78}$-C_2-1[a]	9.146516

[a] One isomer of $Sc_2YN@C_{78}$, whose two Sc atoms are all coordinated to two pairs of fused pentagons.

Table S2. Relative Energies (ΔE, kJ/mol) of $ScY_2N@C_{78}$ Isomers

Species	Δ*E*
$ScY_2N@C_{78}$-D_{3h}	9.713157
$ScY_2N@C_{78}$-C_2	0
$ScY_2N@C_{78}$-C_2-1[b]	4.363889

[b] One isomer of $ScY_2N@C_{78}$, whose one Sc atom is coordinated to one pair of fused pentagons.

Table S3. Relative Energies (ΔE, kJ/mol) of $Sc_3N@C_{78}$ Isomers

Species	Δ*E*
$Sc_3N@C_{78}$-D_{3h}	0
$Sc_3N@C_{78}$-C_2	18.43717

Table S4. Relative Energies (ΔE, kJ/mol) of $Y_3N@C_{78}$ Isomers

Species	Δ*E*
$Y_3N@C_{78}$-D_{3h}	18.00902
$Y_3N@C_{78}$-C_2	0

Table S5. Selected bonding length (Å) in optimized structures of $Sc_3N@C_{78}$-D_{3h}, $Y_3N@C_{78}$-C_2, $Sc_2YN@C_{78}$-D_{3h}, and $ScY_2N@C_{78}$-C_2.

$Sc_3N@C_{78}$- D_{3h}	Sc-cage	2.25	Sc-N	2.01
$Y_3N@C_{78}$- C_2	Y_1-cage	2.43	Y_1-N	2.07
	Y_2-cage	2.49	Y_2-N	2.10
	Y_3-cage		Y_3-N	
$Sc_2YN@C_{78}$- D_{3h}	Y_1-cage	2.39	Y_1-N	2.12
	Sc_2-cage	2.22	Sc_2-N	1.96
	Sc_3-cage		Sc_3-N	
$ScY_2N@C_{78}$- C_2	Sc_1-cage	2.30	Sc_1-N	1.94
	Y_2-cage	2.51	Y_2-N	2.16
	Y_3-cage		Y_3-N	

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