

Supporting Information

Spin-Active Metallofullerene Stabilized by the Core of NC Moiety

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Experimental Section:

1. The synthesis and purification of Sc₃NC@C₈₀

The Sc₃NC@C₈₀-I_h was prepared as reported before.¹ Briefly, the mixture of graphite powder and Sc/Ni₂ alloy with a mass ratio of 1:2 was packed into core-drilled graphite rods. Subsequently the rods were burnt in a Krätschmer-Huffman generator under an atmosphere of 6 Torr N₂ and 194 Torr He. The as-prepared soot was Soxlet-extracted with toluene for 24 h. Sc₃NC@C₈₀ was isolated and purified by multi-step HPLC.¹ Figure S1 and S2 show HPLC data of purified Sc₃NC@C₈₀ sample. MALDI-TOF mass spectrum was also performed to confirm its high purity, see Figure S3.

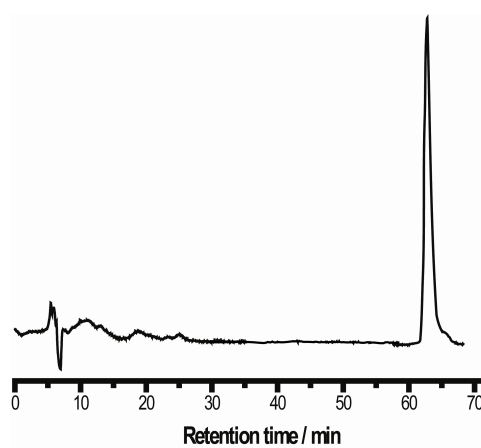


Figure S1. Chromatogram of the isolated Sc₃NC@C₈₀ (20×250 mm Buckyprep column; flow rate 12 mL/min; toluene as eluent).

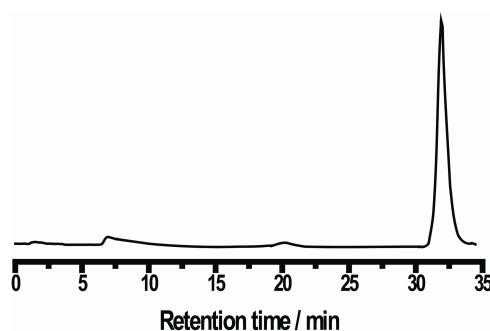


Figure S2. Chromatogram of the isolated Sc₃NC@C₈₀ (20×250 mm Buckyprep-M column; flow rate 12 mL/min; toluene as eluent).

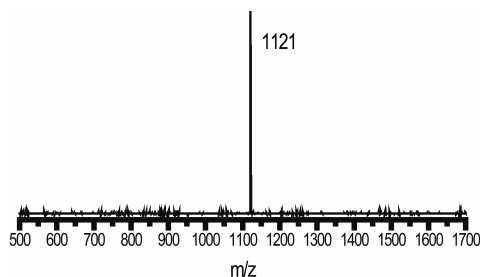


Figure S3. MALDI-TOF mass spectrum of $\text{Sc}_3\text{NC}@C_{80}$.

2. Cyclic voltammogram of $\text{Sc}_3\text{NC}@C_{80}$

Electrochemistry experiments were carried out in *o*-DCB solvent containing 0.05 M $(n\text{-Bu})_4\text{NPF}_6$ with glassy carbon as the working, Pt wire and Ag wire as the counter and reference electrodes, respectively, at a scan rate of 100 mV s^{-1} . The potentials were referred to the $E_{1/2}$ value of the Fc/Fc^+ redox couple measured in the sample solution. Figure S4 shows the CV of $\text{Sc}_3\text{NC}@C_{80}$.

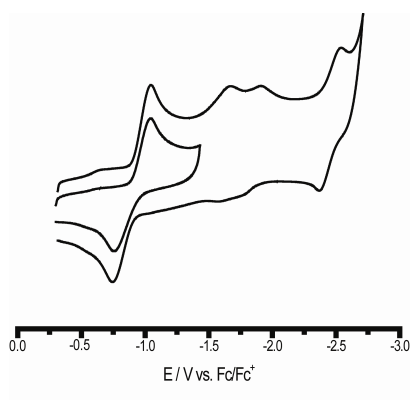


Figure S4. Cyclic voltammogram of $\text{Sc}_3\text{NC}@C_{80}$ (*o*-dichlorobenzene, 0.05 mol/L TBAPF₆, $50 \text{ mV} \cdot \text{s}^{-1}$ scan rate).

3. ESR experiment of $\text{Sc}_3\text{NC}@C_{80}$ anion radical

$\text{Sc}_3\text{NC}@C_{80}$ anion radical was obtained by contacting metal potassium with a solution of $\text{Sc}_3\text{NC}@C_{80}$ in THF for several times.² Subsequently the solution was sealed in a quartz tube after removing oxygen by bubbling nitrogen. ESR experiment was performed on a Bruker ESR spectrometer with continuous wave of X-band at room temperature.

Table S1. The hfcc and g-factor values of several paramagnetic metallofullerenes

Metallofullerenes	a (G)	g
Sc ₃ N@C ₆₈ cation ^{a,b}	1.289	2.0010
Sc ₃ N@C ₈₀ anion ^c	55.6	1.9984
Y ₂ @C ₇₉ N ^d	81.23	1.9740
Sc ₄ O ₂ @C ₈₀ cation ^e	18, 150.4	1.9956
Sc ₄ O ₂ @C ₈₀ anion ^e	2.6, 27.4	1.9960
Sc ₃ C ₂ @C ₈₀ ^f	6.256	2.0006
Sc ₃ NC@C ₈₀ anion	3.890, 1.964	2.0031

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Calculation Section:

All the density functional theory (DFT) computations were performed by using the Dmol3 code^{3,4} with the generalized gradient approximation (GGA) functional of Perdew, Burke, and Ernzerhof (PBE).⁵ For closed- and open-shell systems, the spin-restricted and spin-unrestricted algorithms were used, respectively. All-electron double-numerical basis set with polarization functions (DNP) was applied for all atoms. To take into account relativistic effects, the all-electron scalar relativistic method utilizing the Douglas-Kroll-Hess (DKH) Hamiltonian,^{6,7} which is the most accurate approach available in DMol³ package, was chosen.

Computations of hfc constants with the ORCA package^{8, 9} were performed with two combinations of basis sets. One employed the TZVP {5,3,1}/(11s,6p,1d) basis set¹⁰ for carbon atoms, {5,3,2}/(11s,6p,2d), and Sc, {6,5,4,2}/(17s12p7d2f) (f and g polarization functions were removed from the original def2-TZVP basis for Sc, respectively).

Table S2. Calculated hfcc values of Sc, N, and C nuclei in different internal geometries of $\text{Sc}_3\text{NC@C}_{80}$ anion with ORCA package.

	Sc1	Sc2	Sc3	N	C
$\text{Sc}_3\text{NC@C}_{80}^{\cdot-}$ (N-centered)	-2.60452	-2.32169	-4.45982	-1.117	3.712665
$\text{Sc}_3\text{NC@C}_{80}^{\cdot-}$ (C-centered)	-4.10091	-3.94842	-3.32803	1.349823	-5.96963

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