Supporting Information

Awake N-hyperfine Couplings in Charged Yttrium Nitride Endohedral Fullerenes

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Experimental section:

The empty graphite rods were filled with a mixture of Y/Ni_2 alloy and graphite powder in a weight ratio of 3:2. These rods were then vaporized in a Krätschmer-Huffman generator at 194 Torr He and 6 Torr N_2, the current was kept at 25 A. The resulting soot was Soxlet-extracted with toluene for 12 h. Then the pure $Y_3N@C_{2n}$ (n = 40 - 44) were isolated by multi-stage HPLC separately.

For radicals' ESR experiments, firstly, the $Y_3N@C_{2n}$ (n = 40 - 44) radical samples were carefully dissolved in de-oxygenated tetrahydrofuran(THF) by the vacuum-pumping de-aerating device with a nitrogen-flowing process within ESR tube. Then the tube was blocked by rubber seal and transferred to the ESR spectrometer and performed by repeated contact with K metal in a loop until the ESR signal was appeared. ESR spectra were measured at room temperature using X-band ESR spectrometer (Bruker E500) with continuous-wave X band, the measure power Attention is 13.0 dB, the Frequency is 9.848 GHz. And the spectra were simulated with easyspin package encoded in MATLAB platform. [1]

Computational section:

All conformers of $Y_3N@C_{2n}$ (n = 40 - 44) and related anion radicals were firstly optimized using original pm6 and b3lyp/3-21g* to speed up the computational process, the final optimizations and spin distributions were carried out by B3LYP and TPSSh methods within lanl2de basis for Y and 6-31g* for C, N. The above calculations were performed using the Gaussian 09 quantum chemical program package.[2] Computations of hfcc constants by ORCA package[3] were performed with the open-shell method of UKS at the BP86/TZVP level using RI approximation. The BOMD (Born-Oppenheimer molecular dynamics) calculations were performed in CP2K code[4,5] and employed Velocity Verlet algorithm with the time step of 1 fs at the temperature of 298 K. The trajectories and spin population distributions were computed by the PBE functional and employed Gaussian and Plane Wave (GPW) scheme with Goedecker-Teter-Hutter (GTH) pseudopotentials and DZVP basis set.[5-7] The structures and isosurfaces were visualized with GaussView, the trajectories were visualized with VMD.[8]

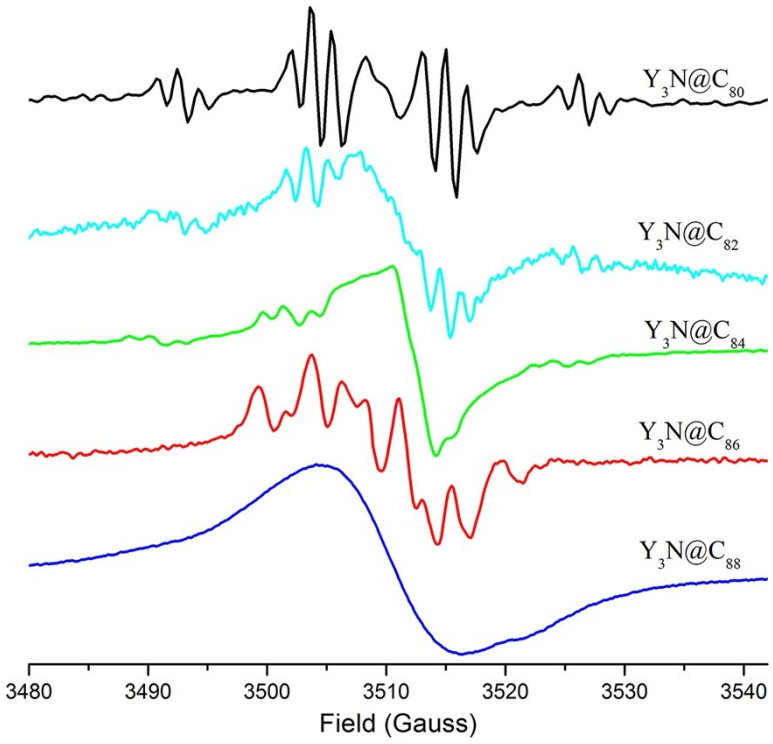

Figure S1. The ESR spectra of the K metal-reduced anion radicals of $Y_3N@C_{2n}$ (N = 40 - 44) in THF at room temperature.

Table S1. The calculated $d_{N\text{-}Y/C\text{-}Y/Y\text{-}Y}$ data. The $d_{N\text{-}Y}$ represents the distance of nitrogen atom and yttrium atom on the Y_3N cluster; the $d_{C\text{-}Y}$ represents the distance of yttrium atom and the nearest carbon atom on the cage, the $d_{Y\text{-}Y}$ represents the distance of yttrium atoms on the Y_3N cluster.

	B3LYP|TPSSh								
	d_{N-Y1}	d_{N-Y2}	d_{N-Y3}	d_{C-Y1}	d_{C-Y2}	d_{C-Y3}	d_{Y1-Y2}	d_{Y2-Y3}	d_{Y1-Y3}
$Y_3N@C_{80}$	2.059|2.059	2.057|2.057	2.058|2.058	2.434|2.435	2.432|2.432	2.431|2.431	3.57|3.57	3.57|3.57	3.56|3.56
$Y_3N@C_{82}$	2.113|2.116	2.081|2.090	2.082|2.089	2.477|2.471	2.385|2.381	2.381|2.381	3.64|3.64	3.61|3.58	3.64|3.64
$Y_3N@C_{84}$	2.124|2.137	2.141|2.149	2.127|2.137	2.541|2.530	2.473|2.469	2.481|2.477	3.83|3.81	3.44|3.43	3.82|3.80
$Y_3N@C_{86}$	2.135|2.143	2.150|2.160	2.157|2.160	2.452|2.441	2.474|2.469	2.484|2.481	3.86|3.83	3.64|3.64	3.68|3.68
$Y_3N@C_{88}$	2.196|2.203	2.172|2.181	2.175|2.179	2.452|2.451	2.474|2.470	2.493|2.491	3.74|3.73	3.75|3.75	3.85|3.85

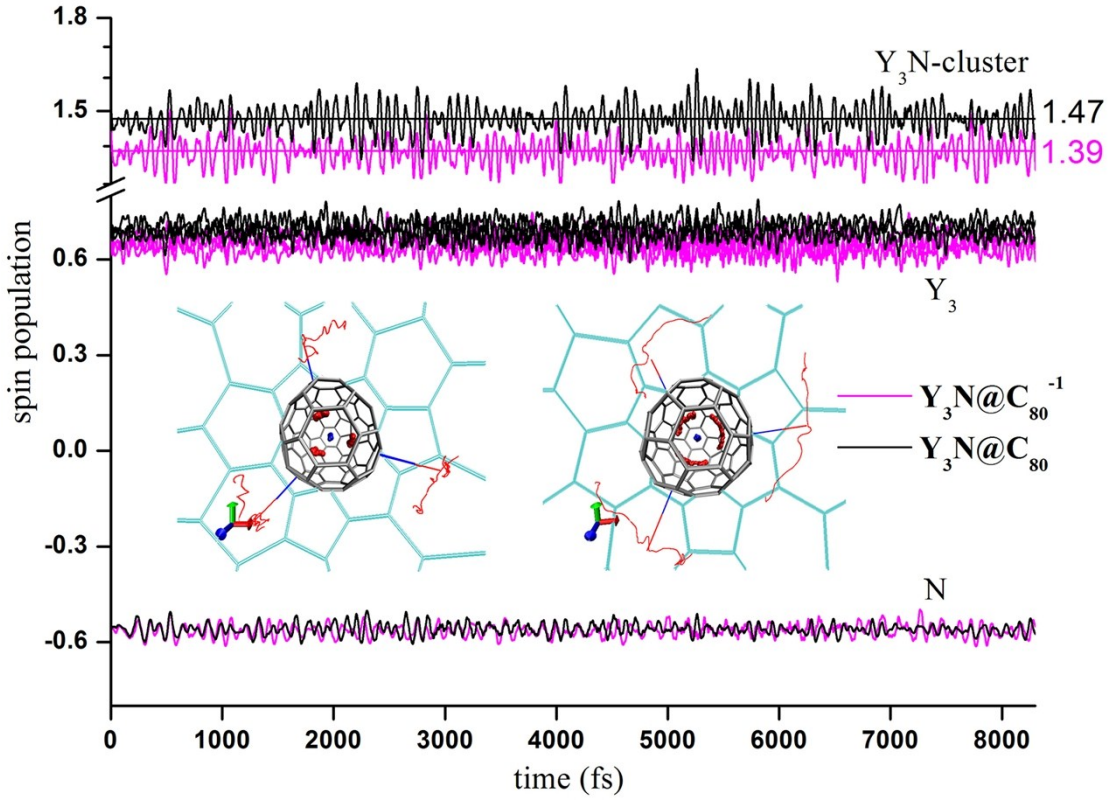

Figure S2. Molecular dynamics simulations (298K) of $Y_3N@C_{80}$ and $Y_3N@C_{80}^-$: Spin populations for the Y_3, N, Y_3N-cluster of neutral (black line) and anion radical (magenta line) of $Y_3N@C_{80}$; trajectories (red for Y, blue for N, gray for carbon cage and light blue for carbon net) of the Y_3N-cluster is in the middle of chart, the central three-dimensional cage spread out to form a two-dimensional nets trajectories. Displacement of the carbon atoms is not shown.

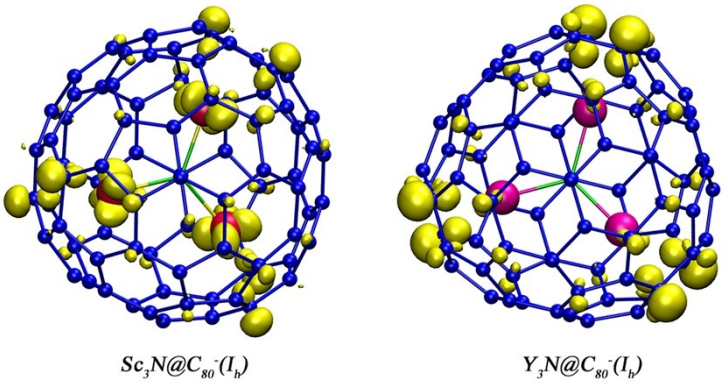

Figure S3. The spin differences of the anion radicals of $Sc_3N@C_{80}(I_h)$ and $Y_3N@C_{80}(I_h)$.

Table S2. The $d_{N\text{-plane}}$ and $\triangle E$ of the clusters $(Y3N)^{6+}$ in the optimized $Y_3N@C_{80}$ to $Y_3N@C_{88}$.

Type	$Sc_3N@C_{80}$	$Y_3N@C_{80}$	$Y_3N@C_{82}$	$Y_3N@C_{84}$	$Y_3N@C_{86}$	$Y_3N@C_{88}$
[a]$d_{N\text{-plane}}$(Å)	0.002	0.008	0.197	0.126	0.057	0.058
△E(kcal/mol)	-	0	-5.07	-14.02	-18.61	-22.87

[a]$d_{N\text{-plane}}$ means the distance of N atom from the plane composed of the three Y atoms.

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