Supporting Information

Awake N-hyperfine Couplings in Charged Yttrium Nitride Endohedral Fullerenes

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Contents

Experimental section: Preparation and characterization of Y₃N@C₂ₙ (n = 40 - 44); the preparation and the ESR measurement of K metal-reduced anion radical of Y₃N@C₂ₙ (n = 40 - 44); the simulation of the ESR spectra of Y₃N@C₁₈₀ and Y₃N@C₁₈₆ anion radicals.

Computational section: DFT-based computations about the structures, hfcc, BOMD, and spin distributions of Y₃N@C₂ₙ (n = 40 - 44).

Figure S1. Experimental ESR spectra of the K metal-reduced anion radicals of Y₃N@C₂ₙ (n = 40 - 44) in THF at room temperature.

Table S1. The calculated d_{N-Y/C-Y/Y} data.

Figure S2. Molecular dynamics simulations (298K) of Y₃N@C₁₈₀ and Y₃N@C₁₈₆⁻.

Figure S3. The spin differences of the anion radicals of Sc₃N@C₁₈₀⁻₁₀ and Y₃N@C₁₈₆⁻₁₀.

Table S2. The d₅₀-plane and ΔE of the clusters (Y₃N)⁶⁺ from Y₃N@C₁₈₀ to Y₃N@C₁₈₆⁻.
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$_3$N@C$_{2n}$ (n = 40 - 44) were isolated by multi-stage HPLC separately.

For radicals’ ESR experiments, firstly, the Y$_3$N@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$_3$N@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 package³ 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 code⁴,⁵ 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.⁶,⁷ 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 $d_{N\text{-}Y}$, $d_{C\text{-}Y}$, and $d_{Y\text{-}Y}$ data. The $d_{N\text{-}Y}$ represents the distance of nitrogen atom and yttrium atom on the Y$_3$N 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$_3$N cluster.

<table>
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<tr>
<th>Species</th>
<th>$d_{N\text{-}Y}$</th>
<th>$d_{C\text{-}Y}$</th>
<th>$d_{Y\text{-}Y}$</th>
<th>$d_{N\text{-}Y}$</th>
<th>$d_{C\text{-}Y}$</th>
<th>$d_{Y\text{-}Y}$</th>
<th>$d_{N\text{-}Y}$</th>
<th>$d_{C\text{-}Y}$</th>
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<td>2.080</td>
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<td>2.493</td>
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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$_3$N@C$_{80}$(I$_h$) and Y$_3$N@C$_{80}$(I$_h$).

Table S2. The $d_{N\text{-plane}}$ and $\Delta E$ of the clusters (Y3N)$^{6^+}$ in the optimized Y$_3$N@C$_{80}$ to Y$_3$N@C$_{88}$.

<table>
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<tr>
<th>Type</th>
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<th>Y$<em>3$N@C$</em>{80}$</th>
<th>Y$<em>3$N@C$</em>{82}$</th>
<th>Y$<em>3$N@C$</em>{84}$</th>
<th>Y$<em>3$N@C$</em>{86}$</th>
<th>Y$<em>3$N@C$</em>{88}$</th>
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<td>$d_{N\text{-plane}}$ (Å)</td>
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<td>-14.02</td>
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<td>-22.87</td>
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</table>

$^a$d$_{N\text{-plane}}$ means the distance of N atom from the plane composed of the three Y atoms.

References

4. CP2K: A general program to perform molecular dynamics simulations. Distributed under the terms of the GNU General Public Licence, https://www.cp2k.org/about).