Supporting Information

Construction of Short Metallofullerene-Peapod with a Spin Probe

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1. Synthesis of $Y_2@C_{79}N$:

Materials: Toluene (HPLC grade); Graphite rod (spectral purity) and Y/Ni_2 alloy (> 99%) were purchased from General Research Institute for Nonferrous Metals (Beijing, China).

Method: The $Y_2@C_{79}N$ was synthesized by the traditional arc-discharging method. In detail, the mixture of graphite powder and Y/Ni_2 alloy with a mass ratio of 1:3 was packed into core-drilled graphite rods. Subsequently the rods were evaporated in a Krätschmer-Huffman generator under an atmosphere of 6 Torr N_2 and 194 Torr He. The as-prepared soot was Soxlet-extracted with toluene for 24 h. $Y_2@C_{79}N$ was isolated and purified by multi-step high performance liquid chromatography (HPLC) as Figure S1. The purity of $Y_2@C_{79}N$ was determined by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS). Figure S1 shows the muti-HPLCs and MALDI-TOF MS profiles of $Y_2@C_{79}N$ sample.

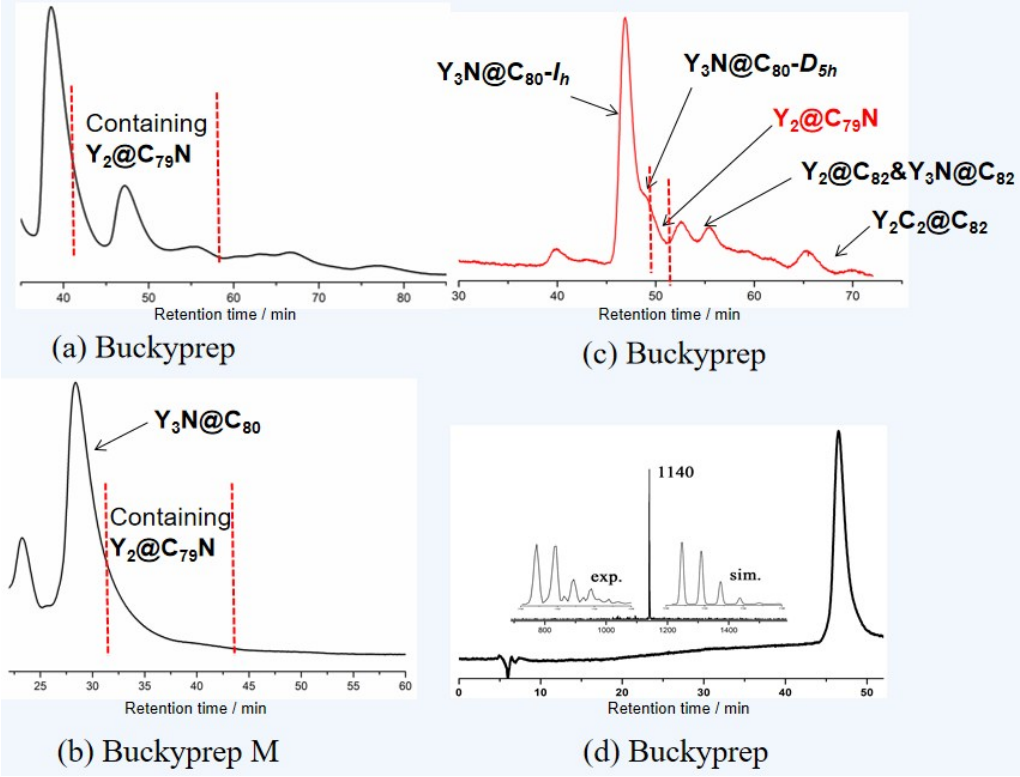

Figure S1. (a-c) Multi-step separation of $Y_2@C_{79}N$ by high performance liquid chromatography (HPLC) using Buckyprep/Buckyprep-M columns; flow rate 12 mL/min; toluene as eluent. (d) Chromatogram of the isolated $Y_2@C_{79}N$ (20×250 mm Buckyprep column; flow rate 12 mL/min; toluene as eluent). The inset shows the experimental and simulated MALDI-TOF MS profiles of $Y_2@C_{79}N$.

2 Synthesis of [4]CHBC: [4]CHBC was synthesized as previous report[1].

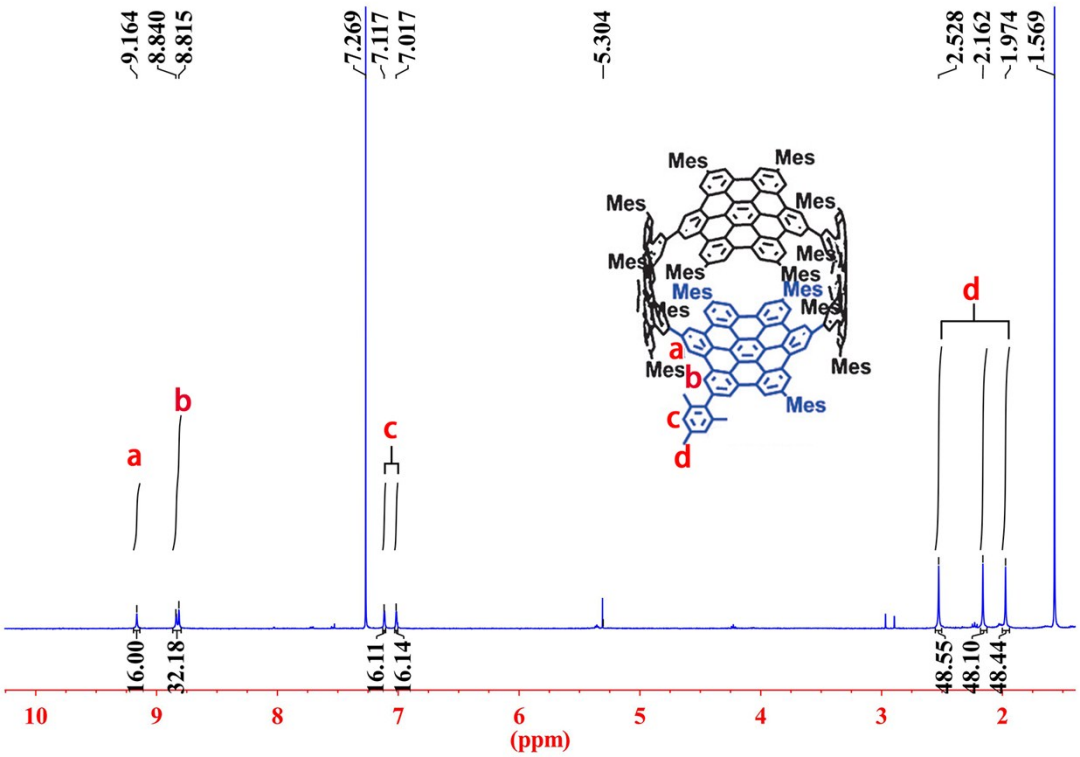

Figure S2. ^{1}H NMR spectrum of [4]CHBC in $CDCl_3$.

3 Synthesis of $Y_2@C_{79}N$ ⊂[4]CHBC: We synthesized the complex at 80 ℃ for 2 h in toluene solution under protected N_2 gas and obtained pure complex by chromatographic separation method.

4 EPR measurement:

All EPR spectra were measured on a Bruker E500 with continuous-wave X band. The frequency was 9.4~9.5 GHz. All of the solution samples were dissolved in CS_2 solution at the same concentration for Figure 4.

Pulsed EPR: Pulsed EPR data were collected on the system by an MS-3 cavity. The low-temperature environment was achieved by liquid helium cryostats (CF935) produced by Oxford Instruments. The measurement temperatures were stabilized for 30 min before the measurements were carried out. The T_1 values were measured by the inversion recovery method. The T_m values were obtained by increasing the τ value of the Hahn echo sequence.

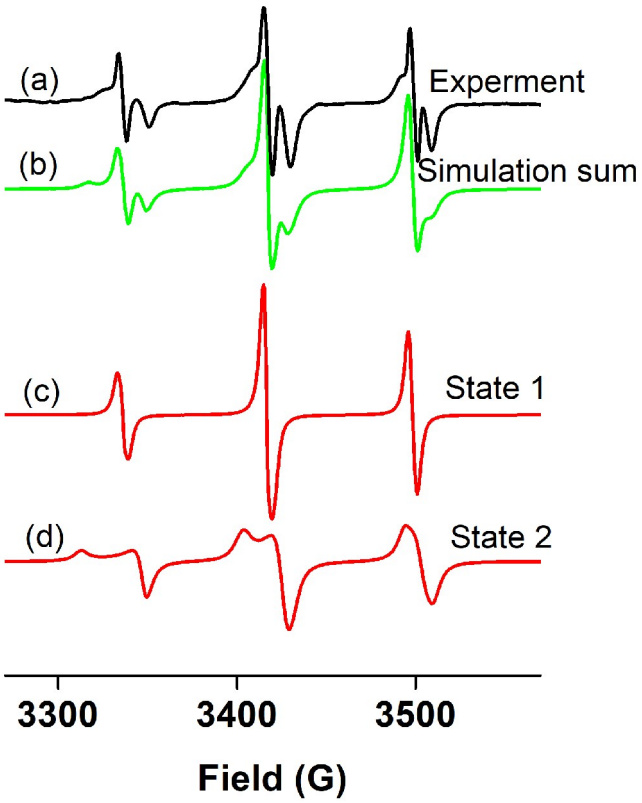

Figure S3 (a) Experimental spectrum of $Y_2@C_{79}N⊂$[4]CHBC at 233 K. (b) Sum of the simulated spectra of the two different states for $Y_2@C_{79}N⊂$[4]CHBC. Simulated spectra of (c) state 1 and (d) state 2.

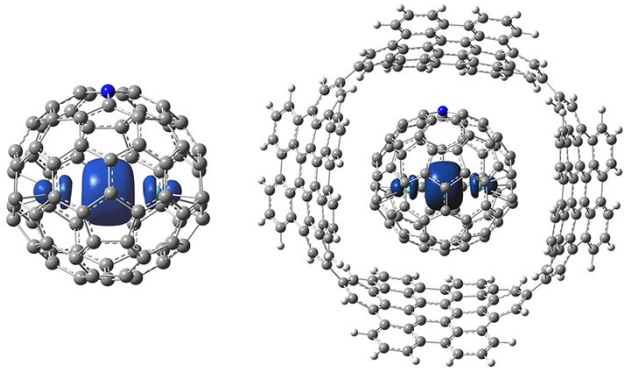

Figure S4 Spin distributions of $Y_2@C_{79}N$ (left) and $Y_2@C_{79}N⊂$[4]CHBC (right).

6 Theoretical Section: $Y_2@C_{79}N$ and $Y_2@C_{79}N⊂$[4]CHBC were firstly optimized using original PM6 and B3LYP/3-21g* to speed up the computational process, the final optimizations and the energy profiles corresponding to the movement of $Y_2@C_{79}N$ were carried out by B3LYP-D3 methods within lanl2de basis for Y and 6-31g* for C, H and N,

here the Grimme's DFT-D3 method provides an empirical dispersion correction. The above calculations were using the Gaussian 09 quantum chemical program package. The structures and isosurfaces were visualized with GaussView. The simulations of the EPR spectra were carried out by the EasySpin package (http://www.easyspin.org) on the Matlab platform.

1. D. Lu, G. Zhuang, H. Wu, S. Wang, S. Yang and P. Du, *Angewandte Chemie*, 2017, **129**, 164-168.