Supporting Information

Spin-Paramagnet Communication between Nitroxide Radical and Metallofullerene

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Experimental Section:

1. The synthesis and purification of $DySc_2N@C_{80}$, $Dy_2ScN@C_{80}$ and $Sc_3N@C_{80}$.

Graphite rods were core-drilled and subsequently packed with a mixture of Sc/Ni_2, Dy/Ni_2 alloy and graphite powder in a weight ratio of Sc: Dy: C = 3: 12: 1. These rods were then vaporized in a Krätschmer-Huffman generator at 194 Torr He and 6 Torr N_2. The resulting soot was Soxlet-extracted with toluene for 24 h. The target products were isolated from various empty fullerenes and other scandium metallofullerenes by HPLC.

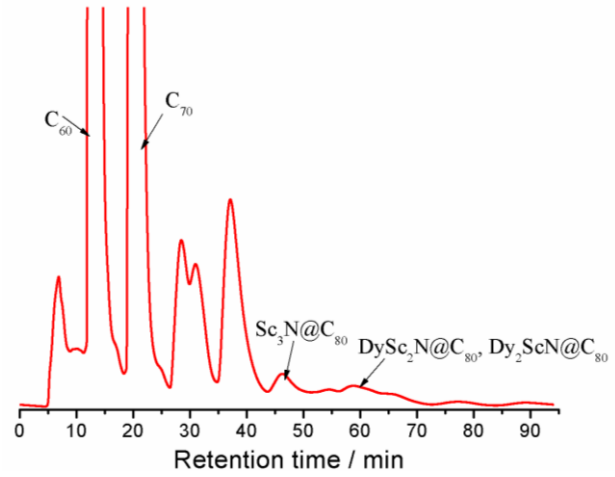

Figure S1. The first stage HPLC profile of toluene extract of the soot containing endohedral metallofullerenes (20 × 250 mm Buckyprep column; flow rate 12 mL/min; toluene as eluent). $DySc_2N@C_{80}$, $Dy_2ScN@C_{80}$ and $Sc_3N@C_{80}$ containing fraction were collected and enriched, following a multistage HPLC technique to isolate and purify the target products.

2. HPLC data of purified $DySc_2N@C_{80}$, $Dy_2ScN@C_{80}$ and $Sc_3N@C_{80}$.

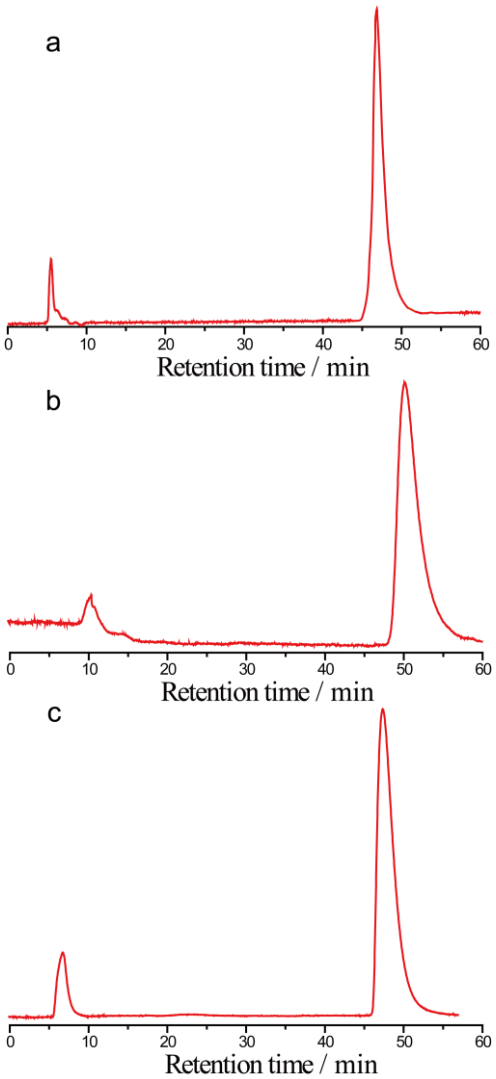

Figure S2. Chromatograms of the isolated **a**, $DySc_2N@C_{80}$, **b**, $Dy_2ScN@C_{80}$ and **c**, $Sc_3N@C_{80}$ after purified by the multistage HPLC technique. HPLC conditions: 10 × 250 mm Buckyprep column, 12 mL/min flow rate with toluene, 330 nm detection.

3. MALDI-TOF mass spectra of purified $DySc_2N@C_{80}$, $Dy_2ScN@C_{80}$ and $Sc_3N@C_{80}$.

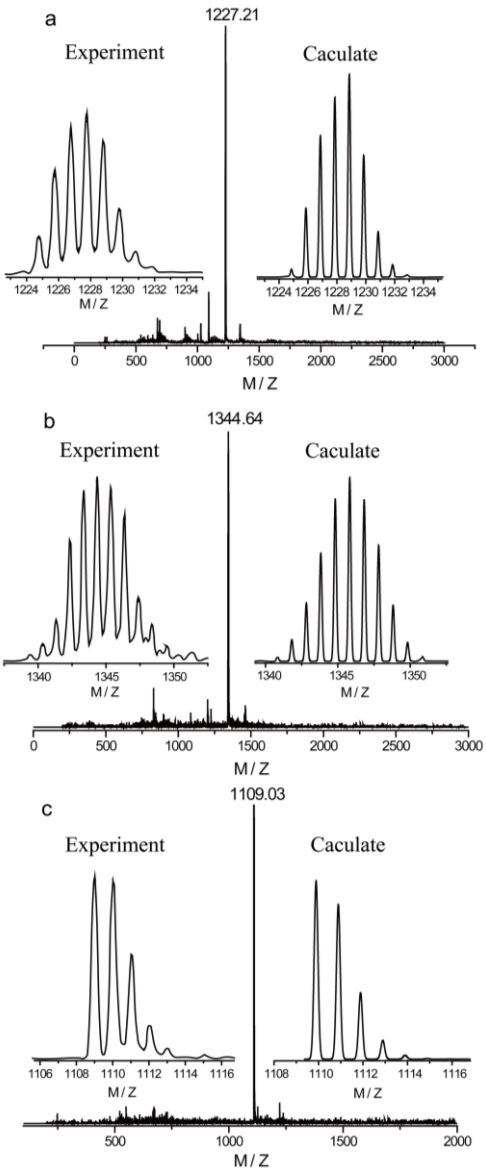

Figure S3. MALDI-TOF mass spectra of purified **a**, $DySc_2N@C_{80}$, **b**, $Dy_2ScN@C_{80}$ and **c**, $Sc_3N@C_{80}$. The insets show the experimental and calculated isotope distributions of $DySc_2N@C_{80}$, $Dy_2ScN@C_{80}$ and $Sc_3N@C_{80}$.

4. UV/Vis-NIR spectra of purified $DySc_2N@C_{80}$, $Dy_2ScN@C_{80}$ and $Sc_3N@C_{80}$.

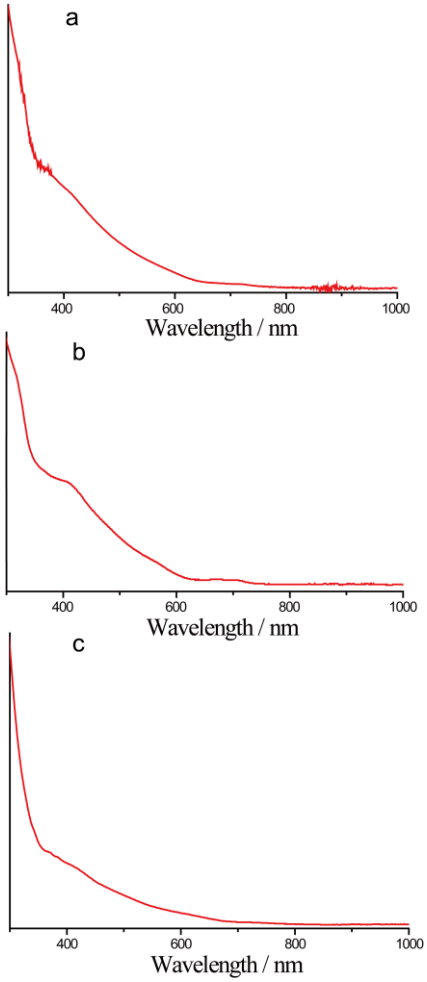

Figure S4. UV/Vis-NIR spectra of purified **a**, $DySc_2N@C_{80}$, **b**, $Dy_2ScN@C_{80}$ and **c**, $Sc_3N@C_{80}$ in toluene.

5. The synthesis and purification of $DySc_2N@C_{80}$, $Dy_2ScN@C_{80}$ and $Sc_3N@C_{80}$ derivatives.

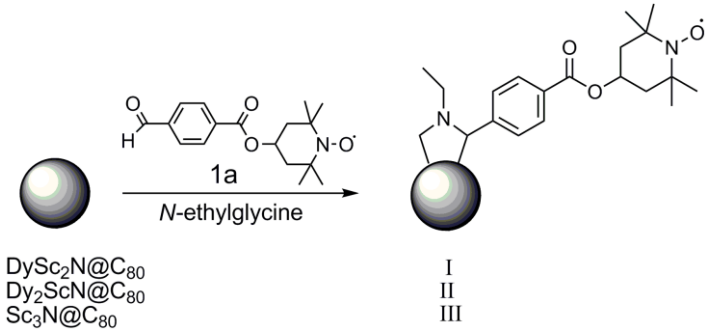

Figure S5. The synthesis procedure of I, II and III.

6. HPLC data of purified $DySc_2N@C_{80}$, $Dy_2ScN@C_{80}$ and $Sc_3N@C_{80}$ derivatives.

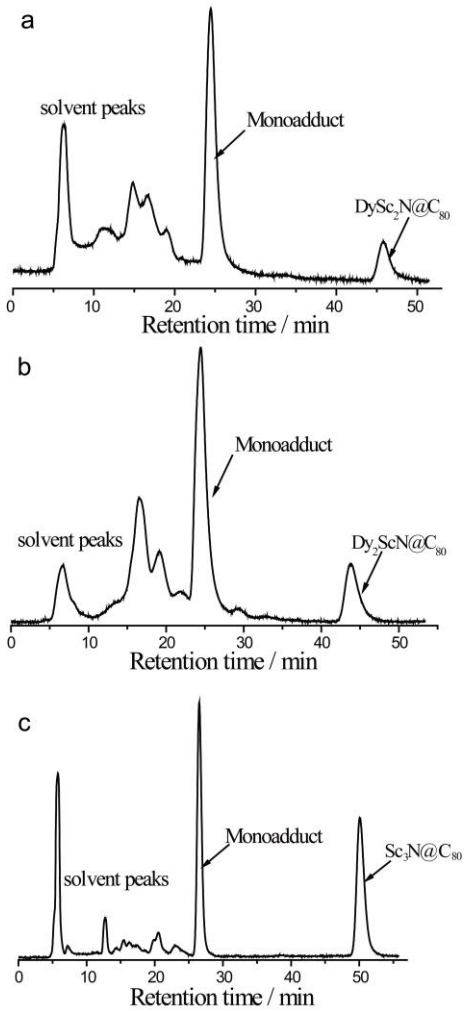

Figure S6. HPLC profiles of the cycloaddition of **a**, I, **b**, II and **c**, III. HPLC conditions: 10 × 250 mm Buckyprep column, 12 mL/min flow rate with toluene, 330 nm detection.

7. The UV/Vis-NIR spectra of $DySc_2N@C_{80}$, $Dy_2ScN@C_{80}$ and $Sc_3N@C_{80}$ derivatives.

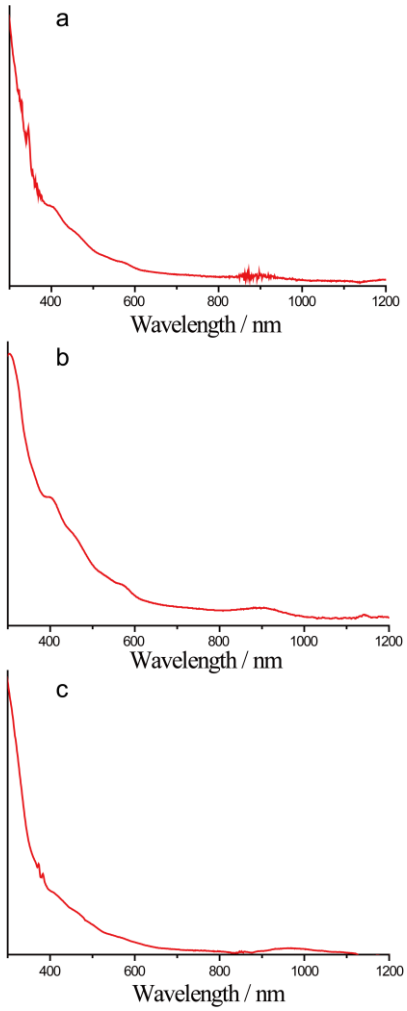

Figure S7. UV/Vis-NIR spectra of purified **a**, I, **b**, II and **c**, III in toluene.

8. The ESR spectra of $DySc_2N@C_{80}$, $Dy_2ScN@C_{80}$ and $Sc_3N@C_{80}$ derivatives.

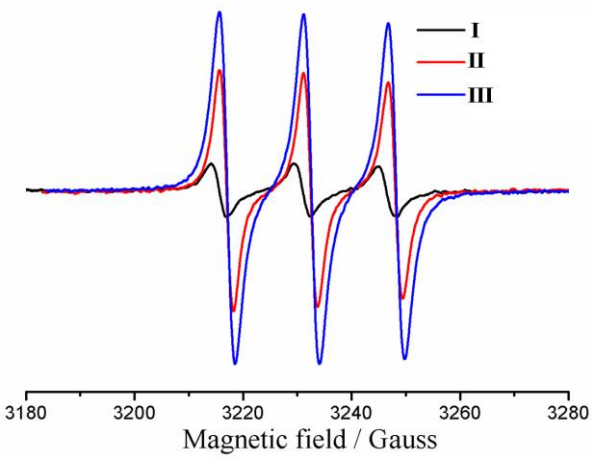

Figure S8. The ESR spectra of I, II and III at the same concentration at room temperature in toluene solution.