Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

Magnetoreception System Constructed by Dysprosium Metallofullerene and Nitroxide Radical

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Contents

1. Synthesis methods

1-1. Synthesis of $Dy_3N@C_{80}$, $Sc_3N@C_{80}$ and $Y_3N@C_{80}$

$Dy_3N@C_{80}$, $Sc_3N@C_{80}$ and $Y_3N@C_{80}$ were synthesized by arc-discharging method. Graphite rods were core-drilled and susequently packed with a mixture of Dy/Ni_2, Sc/Ni_2, Y/Ni_2 and graphite powder in a weight ration of Dy:C = 4:1, Sc:C= 3:1, Y:C= 4:1, respectively. 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 by high-performance liquid chromatography (HPLC) using Buckyprep column, together with results of MALDI-TOF MS analysis, as shown in Figure S1, S2 and S3.

1-2. Synthesis of derivatives containing nitroxide radical of $Dy_3N@C_{80}$, $Sc_3N@C_{80}$ and $Y_3N@C_{80}$

$Dy_3N@C_{80}$, $Sc_3N@C_{80}$ and $Y_3N@C_{80}$ were heated with N-ethylglycine and 1-oxy-2,2,6,6-teramethylpiperidin-4-yl 1-acetylpiperidine-4-carboxylate, which was synthesized as described in literature methods[1] at 120 °C, to give corresponding fullerene derivatives containing nitroxide radical with yields of nearly 70% in toluene solution for 50 min, respectively. Pure derivatives were isolated by high-performance liquid chromatography (HPLC) using Buckprep column.

1-3. Synthesis of $Sc_3N@C_{80}$PNOH

To a solution of ~0.5 mg of the nitroxide derivative $Sc_3N@C_{80}$PNO· in ~2 ml toluenewas added ~1 mg *p*-Toluenesulfonohydrazide, and stirred under air for about 15min.

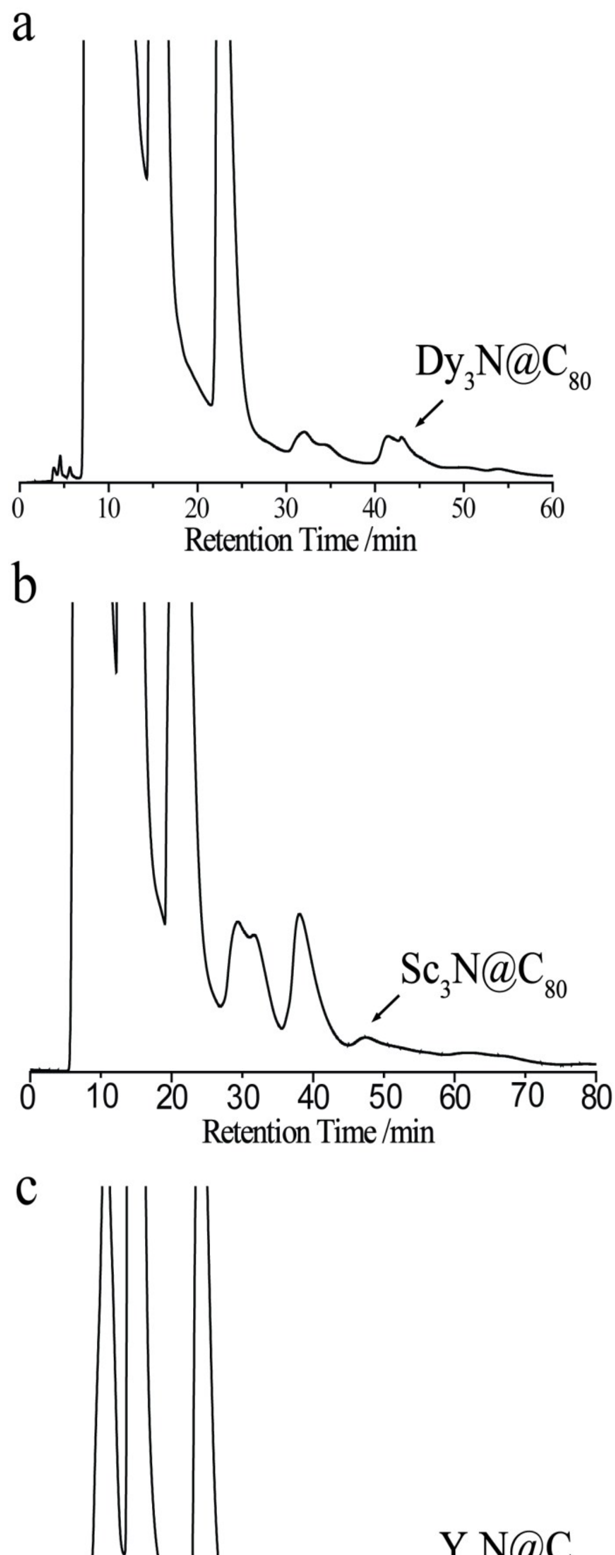
2. Characterizations methods of fullerenes and their derivatives

UV/vis-NIR spectra of purified metallofullerenes and their derivatives were collected on Lambda 950 UV/vis/NIR Spectrometer (PerkinElmer Instruments). ESR spectra were measured on a JEOL JEF FA200 X-band spectra. The samples were degassed and the oxygen was removed from the solutions. All of the samples were dissolved in toluene solution at the same concentration. ^{1}H NMR spectra of $Sc_3N@C_{80}$PNO· was measured in chloroform-*d* on a Brucker 600 MHz spectrometer (Figure S4). The static magnetization was measured with a Quantum Design MPMS XL-7 system between 2 and 300 K in magnetic fields up to 0.1 T. The net mass of the samples is in the μg range. The samples were measured in a capsule with negligible magnetism.

3. Theoretical calculation on $Y_3N@C_{80}$PNO· regioisomers

Density functional theory (DFT) computations were performed using the Gaussian 09 program package. The [5,6] and [6,6] isomers of $Y_3N@C_{80}$ were optimized at the UB3LYP method with a pseudopotential lanl2dz basis set for yttrium atoms and a 6-31G* basis set for carbon, nitrogen and oxygen atoms.

4. Supporting figures



a
$Dy_3N@C_{80}$
0 10 20 30 40 50 60
Retention Time /min
b
$Sc_3N@C_{80}$
0 10 20 30 40 50 60 70 80
Retention Time /min
c
$Y_3N@C_{80}$
0 10 20 30 40 50 60
Retention Time /min

Fig S1. The first stage HPLC of toluene extract of the soot containing endohedral metallofullerenes (20 × 250 mm Buckyprep column; flow rate 12 mL/min; toluene as eluent). (a) $Dy_3N@C_{80}$, (b) $Sc_3N@C_{80}$ and (c) $Y_3N@C_{80}$.

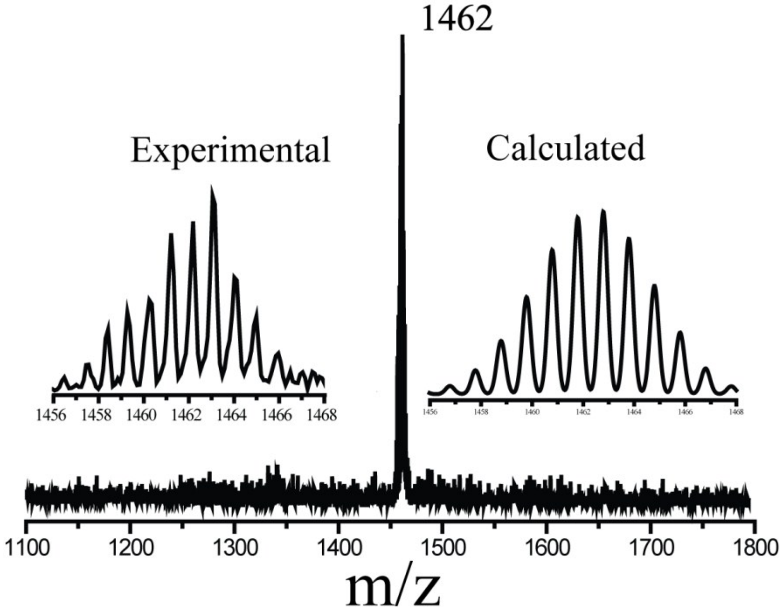


Fig S2. MALDI-TOF mass spectra of purified $Dy_3N@C_{80}$. The insets show the experimental and calculated isotope distributions of $Dy_3N@C_{80}$.

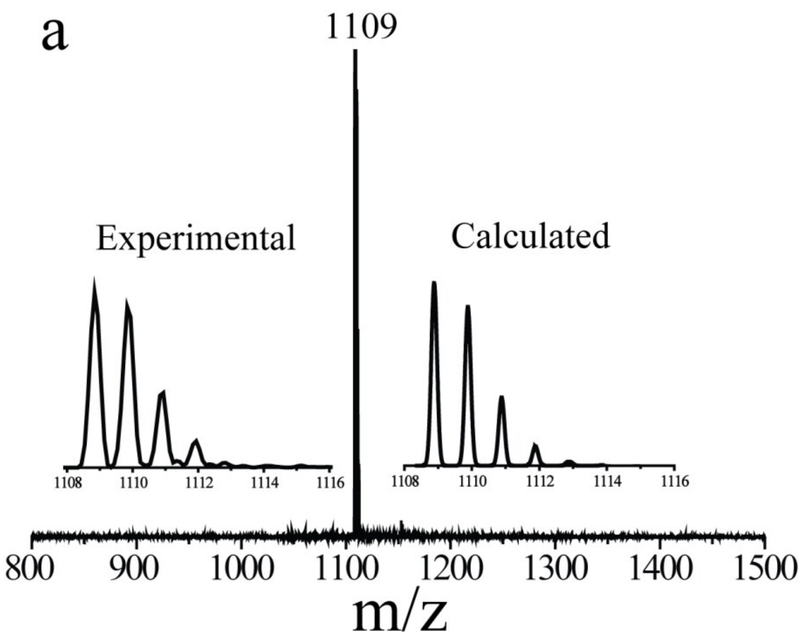


Fig S3. MALDI-TOF mass spectra of purified (a) $Sc_3N@C_{80}$ and (b) $Y_3N@C_{80}$. The insets show the experimental and calculated isotope distributions of $Sc_3N@C_{80}$ and $Y_3N@C_{80}$.

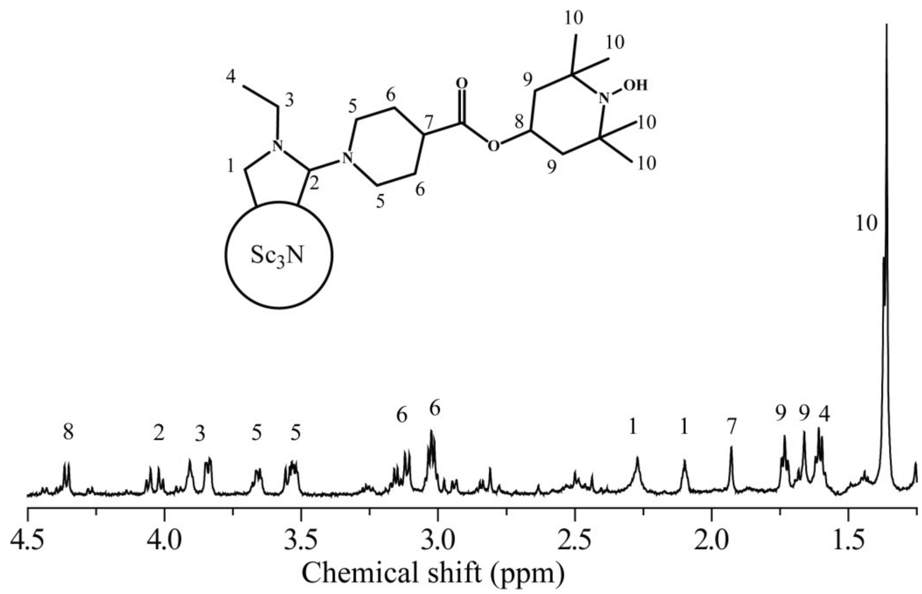


Figure S4. ^{1}H NMR spectra of $Sc_3N@C_{80}PNOH$. The ^{1}H NMR spectra of $Sc_3N@C_{80}PNOH$ between 1.2 and 4.5 ppm at 600 MHz in chlorlform-*d* ($CDCl_3$) at 293 K.

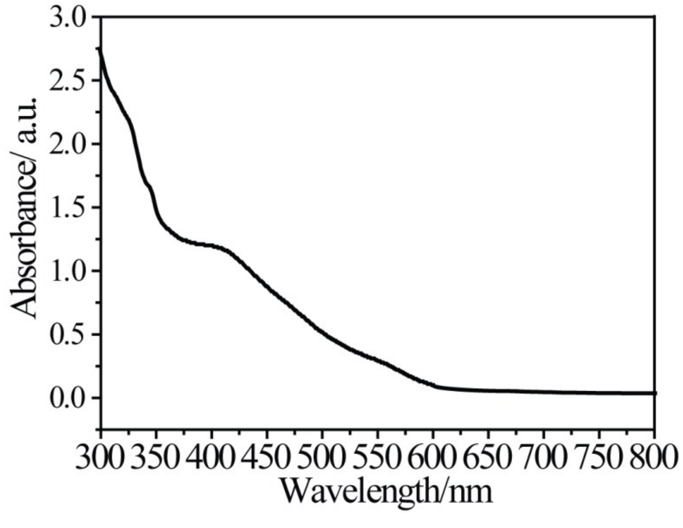


Fig S5. UV/Vis-NIR spectra of purified $Dy_3N@C_{80}$-I_h in toluene.

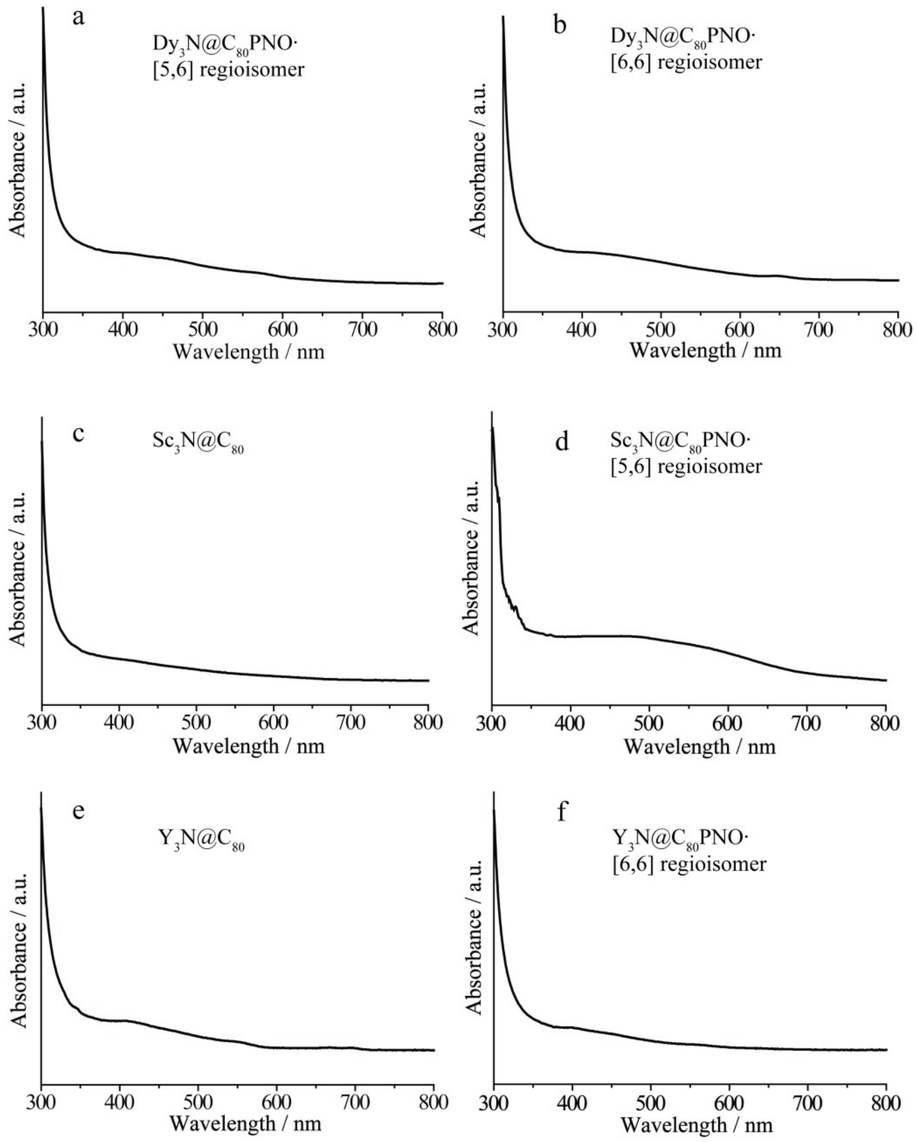
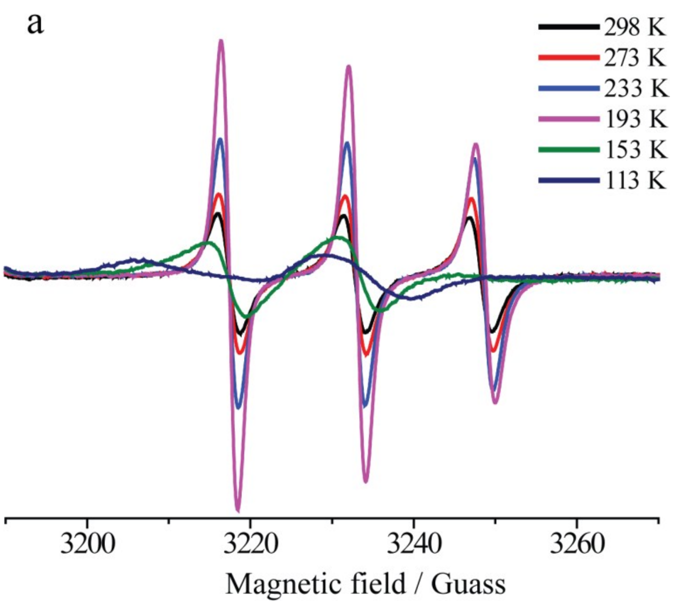


Fig S6. UV/Vis-NIR spectra of (a) [5,6], (b) [6,6] isomers of $Dy_3N@C_{80}PNO^{\bullet}$,(c) $Sc_3N@C_{80}$, (d) [5,6] isomers of $Sc_3N@C_{80}PNO^{\bullet}$, (e) $Y_3N@C_{80}$ and (f) [6,6] isomers of $Y_3N@C_{80}PNO^{\bullet}$ in toluene.



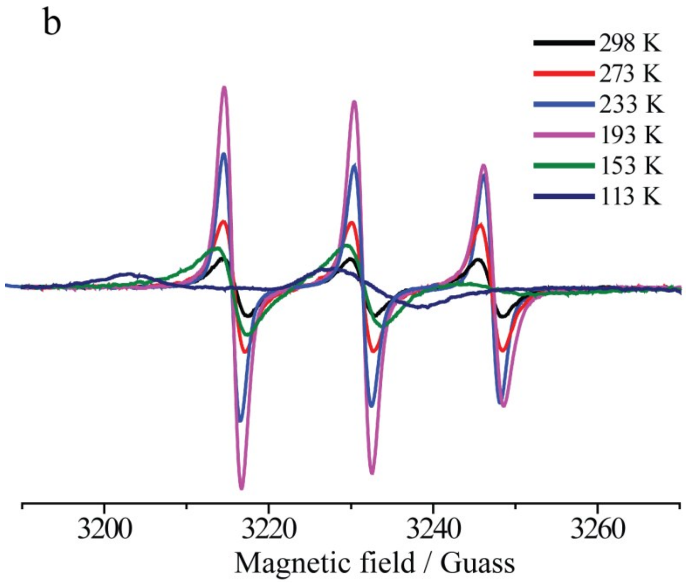


Fig S7. The ESR spectra of [5,6] and [6,6] isomers of $Dy_3N@C_{80}PNO^{\bullet}$ at variable temperature in toluene solution.

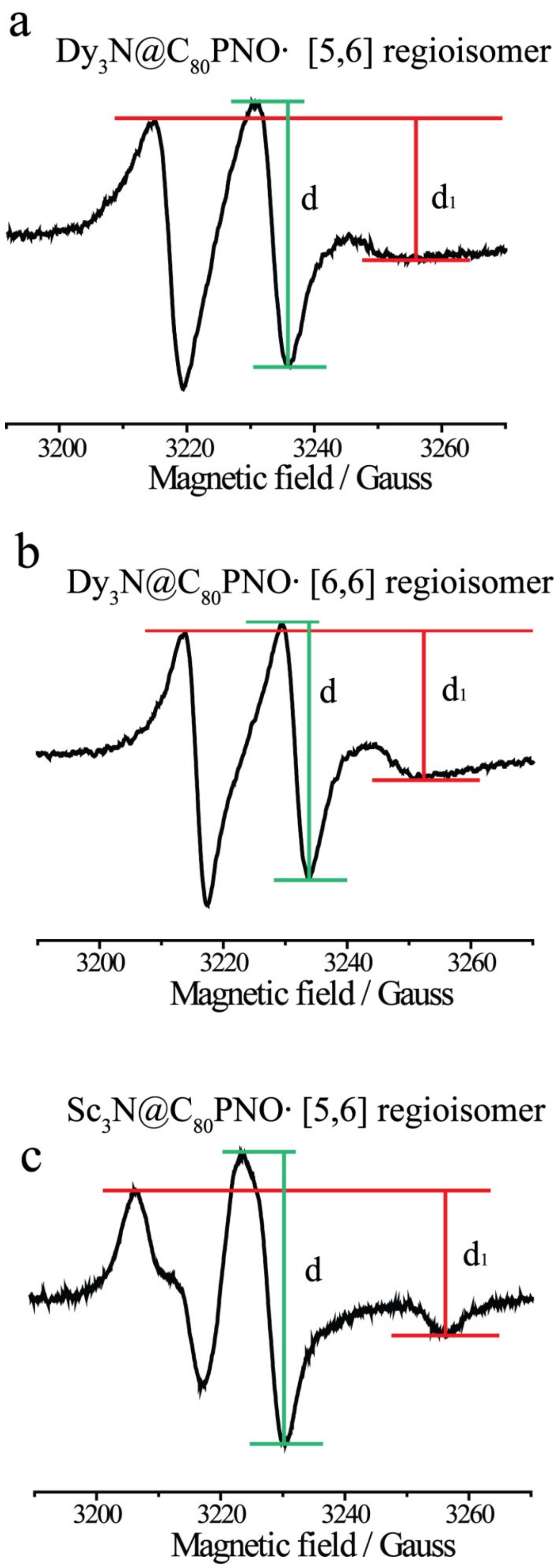


Fig S8. ESR spectra of (a) $Dy_3N@C_{80}PNO^{\bullet}$ [5,6] regioisomer, (b) $Dy_3N@C_{80}PNO^{\bullet}$ [6,6]

regioisomer and (c) $Dy_3N@C_{80}PNO^{\bullet}$ [6,6] regioisomer at 153 K.

Table 1: Parameter d_1/d of the different paramagnetic system at 153K.

Sample	d_1/d
$Dy_3N@C_{80}PNO^{\bullet}$ [6,6] regioisomer	0.60
$Dy_3N@C_{80}PNO^{\bullet}$ [5,6] regioisomer	0.53
$Sc_3N@C_{80}PNO^{\bullet}$ [5,6] regioisomer	0.51

References:

1. Li, Y. J.; Lei, X. G.; Lawler, R. G.; Murata, Y.; Komatsu, K and Turro, N. J. D. *J. Phys. Chem. Lett.* 2010**, 1** , 2135-2138.