Cluster-size dependent internal dynamics and magnetic anisotropy of Ho ions in HoM$_2$N@C$_{80}$ and Ho$_2$MN@C$_{80}$ families (M = Sc, Lu, Y)

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Synthesis

Ho/Lu and Ho/Y MMNCFs were synthesized by the “selective organic solid” (SOS) route as described previously. Briefly, a mixture of Ho\textsubscript{2}O\textsubscript{3}, Y\textsubscript{2}O\textsubscript{3} or Lu\textsubscript{2}O\textsubscript{3} (99.9%, MaTeck GmbH, Germany), guanidine thiocyanate (GT) and graphite powder was used (molar ratio Ho/M/GT/C=1/1/2.5/15, M= Lu or Y). After dc-arc discharging, the soot was pre-extracted by acetone and further Soxhlet-extracted by CS\textsubscript{2} for 20h.

Isolation and Characterization

The isolation of Ho-based MMNCFs was performed by two-step HPLC. At the first step a linear combination of two analytical 4.6×250 mm Buckyprep columns (Nacalai Tesque, Japan) was applied on a Hewlett-Packard instrument (series 1100) with toluene as the eluent. Further isolation was performed by a recycling HPLC (Sunchrom, Germany) using a Buckyprep column (10×250 mm; Nacalai Tesque, Japan) and toluene as the eluent. The UV detector set to 320 nm was employed for fullerene detection for all steps. The details of HPLC isolation of Ho-based MMNCFs are described in the Supporting Information. The purity of the isolated products was checked by laser desorption/ionization time-of-flight (LDI-TOF) mass spectrometry (Biflex III, Bruker, Germany), the spectra are shown in supporting information as well. UV-Vis-NIR absorption spectra were measured in toluene solution using Shimadzu 3100 spectrometer.

1.1 Synthesis and isolation of Ho\textsubscript{x}Y\textsubscript{3−x}N@C\textsubscript{80} (x=1, 2)
Figure S1. Chromatogram of a raw Ho$_x$Y$_{3-x}$N@C$_{2n}$ fullerenes extract synthesized by the “selective organic solid” method (linear combination of two 4.6×250 mm Buckyprep columns, flow rate 1.6 ml/min, injection volume 200 µL, toluene as mobile phase, 40 °C). The inset shows the enlarged chromatographic region of 29.5-34.5 min.

Figure S2. The HPLC isolation of fraction Fr 3. (10×250 mm Buckyprep column; flow rate 1.5 ml/min; injection volume 5 ml; toluene as eluent; 20 °C).

The synthesis of Ho$_x$Y$_{3-x}$N@C$_{80}$ ($x = 1, 2$) was achieved by “selective organic solid” route. The process of dc-arc discharging and solution extraction was the same in the production of Ho$_x$Sc$_{3-x}$N@C$_{80}$ (I; $x=1, 2$). A mixture of Ho$_2$O$_3$ and Y$_2$O$_3$ (99.9%, MaTeck GmbH, Germany), guanidine thiocyanate (GT) and graphite powder was used (molar ratio Ho/Y/GT/C=1:1:2.5:15). The chromatogram of the extracted Ho$_x$Y$_{3-x}$N@C$_{2n}$ fullerenes is shown in Figure S1. The Ho$_x$Y$_{3-x}$N@C$_{80}$ (I, $x = 1, 2$) were isolated by multistep HPLC (see Figure S2-5). Firstly, the analytical HPLC was employed to collect Ho$_x$Y$_{3-x}$N@C$_{80}$ (I) (Fraction 3) and Ho$_x$Y$_{3-x}$N@C$_{80}$ (II) (Fraction 4) respectively. Different to Ho$_x$Sc$_{3-x}$N@C$_{80}$ (I, $x = 1, 2$), the retention time of Ho$_x$Y$_{3-x}$N@C$_{80}$ (I) in Buckyprep column (4.6×250 mm) are identical. Secondly, the Fr 3 was subjected to isolation by recycling HPLC on a Buckyprep column (10×250 mm), see Figure S2. After 12 cycles, four sub-fractions could be obtained which marked as Fr 31 to Fr 34. The relative yield of Ho$_x$Y$_{3-x}$N@C$_{80}$ ($x = 0-3$) could be estimated from the integrated areas of the corresponding chromatographic peaks which agrees well with mass spectrum result of Fr 3 (Figure S2b).
Isolation of HoY$_2$N@C$_{80}$ (I) was accomplished by removing the small amount of Y$_3$N@C$_{80}$ (I) and Ho$_2$YN@C$_{80}$ (I) from fraction 32 after 30 cycles. Similarly, the pure Ho$_2$YN@C$_{80}$ (I) could be obtained by removing the minor structures (HoY$_2$N@C$_{80}$ (I) and Ho$_3$N@C$_{80}$ (I)) in fraction 33 through 27 cycles. The purity of Ho$_x$Y$_{3-x}$N@C$_{80}$ (I, x = 1, 2) were confirmed by LDI-TOF mass spectroscopy (Figure S5).
The isolated samples of Ho$_x$Y$_{3-x}$N@C$_{80}$ (I; $x=1, 2$) were identified by laser-desorption/ionization time-of-flight (LDI-TOF) mass spectrum analysis, which confirmed their high purity.

1.2 Synthesis and isolation of Ho$_x$Lu$_{3-x}$N@C$_{80}$ (I, $x=1, 2$)

The synthesis of Ho$_x$Lu$_{3-x}$N@C$_{80}$ ($x=1, 2$) was achieved by “selective organic solid” route as.

A mixture of Ho$_2$O$_3$ and Lu$_2$O$_3$ (99.9%, MaTeck GmbH, Germany), guanidine thiocyanate (GT) and graphite powder was used (molar ratio Ho/Lu/GT/C=1:1:2.5:15).
The mixture of Ho$_x$Lu$_{3-x}$N@C$_{28}$ was subjected to isolation by analytical HPLC in the first step (Figure S6). Ho$_x$Lu$_{3-x}$N@C$_{80}$ (I) and Ho$_x$Lu$_{3-x}$N@C$_{80}$ (II) were separated into Fr 1 (28.0-29.9 min) and Fr 2 (29.9-31.5 min) respectively according to the difference of their cage symmetry. In the second step, three sub-fractions could be obtained after recycling fraction 1 over 30 times which then named as Fr 11, Fr 12 and Fr 13. Checking by mass spectrum, the dominant structure in Fr 12 is Ho$_x$Lu$_{3-x}$N@C$_{80}$ (I) (Figure S7). In the third step, the Fr 12 was subjected to recycling HPLC again for removing minor structures (HoLu$_2$N@C$_{80}$ (I) and Ho$_2$N@C$_{80}$ (I)). As shown in Figure S8, Fr 122 was collected after 44 cycles. In the fourth step, after running another 44 cycles, the isolation of Ho$_2$LuN@C$_{80}$ (I) was successfully achieved and its purity was confirmed by LDI-TOF mass spectroscopy (Figure S11).
Similar to Ho$_2$Lu@C$_{80}$ (I), the isolation of HoLu$_2$N@C$_{80}$ (I) is extremely time-consuming due to the retention time of Lu$_3$N@C$_{80}$ (I) and HoLu$_2$N@C$_{80}$ (I) is almost identical. Only by running on recycling HPLC over 73 cycles, small amount of HoLu$_2$N@C$_{80}$ (I) could be obtained, see Figure S10. The purity of HoLu$_2$N@C$_{80}$ (I) was confirmed by LDI-TOF mass spectroscopy (Figure S11).
Figure S10. The isolation of fraction Fr 121. (10×250 mm Buckyprep column; flow rate 1.5 ml/min; injection volume 5 ml; toluene as eluent; 20 °C).

Figure S11. The isolated samples of Ho$_x$Lu$_{3-x}$N@C$_{80}$ (I; $x=1, 2$) were identified by LDI-TOF mass spectrum analysis, which confirmed their high purity.
2. Spectroscopic properties of $\text{Ho}_x\text{M}_{3-x}\text{N@C}_{80}$ ($\text{I; M= Y and Lu; } x=1, 2$)

2.1 UV-vis-NIR spectra of $\text{Ho}_x\text{M}_{3-x}\text{N@C}_{80}$

![Fig S12. UV-vis-NIR spectra of Ho$_x$Y$_{3-x}$N@C$_{80}$ (I; $x=0–3$) (left) and Ho$_x$Lu$_{3-x}$N@C$_{80}$ (I; $x=0–3$) (right) in toluene.](image)

2.2 FTIR spectra of $\text{Ho}_x\text{M}_{3-x}\text{N@C}_{80}$ ($\text{I; x=0–3}$)

![Fig S13. FTIR spectra of Ho$_x$M$_{3-x}$N@C$_{80}$ (I; M= Y, Lu; $x=0–3$) compared with Ho$_x$Sc$_{3-x}$N@C$_{80}$.](image)
3. Quantum chemical calculations

B3LYP calculations were performed using the Firefly code.\(^1\) The basis set was def2-SVP\(^2\) for carbon atoms, def2-TZVP\(^2\) for nitrogen, Stuttgart-Cologne effective core potentials for Sc (ECP10MDF)\(^3\) with \{3,1,1,1,1/2,2,1,1/4,1,1/1,1/1\} valence part, ECP28MWB\(^4,5\) for Y with \{3,1,1,1/4,1,1/4,1/1\} valence electron part, and 4f-in-core ECP56MWB-II for Ho with \{3,1,1,1/3,1,1,1/2,1,1,1/1,1/1,1/1\} valence part.\(^6\)

For QTAIM calculations, computations were performed using ORCA,\(^7\) PBE functional, DKH relativistic correction, and DKH-TZVP full electron basis set.\(^8\)


Correlation between $\Delta \chi$ (arb. unts) and Ho-Sc distance. The fitted polynomial was used to compute $\Delta \chi$ at any point of the MD trajectory.