Supporting Information for:

The Role of an Asymmetric Nitride Cluster on Fullerene Cage: the Non-IPR

Endohedral DySc₂N@C₇₆

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S5. Comparison of the computed IR spectra of selected most stable isomers of YSc₂N@C₇₆ to the experimental spectrum of DySc₂N@C₇₆

S1. Isolation of DySc₂N@C₇₆:

A typical chromatogram of a Dy_xSc_{3-x}N@C_{2n} fullerene extract mixture obtained on two Buckyprep columns is shown in Scheme S1-I. Together with mass-spectroscopic (MS) analysis it shows that Dy_xSc_{3-x}N@C_{2n} clusterfullerenes (fractions A-D) are the dominant products. The first-step HPLC results in isolation of fraction **B**, which is subject to the second-step isolation by recycling HPLC (Buckyprep column) and fraction **B-1** was collected (Scheme S1-II).

In the third-step isolation by recycling HPLC (Buckyprep column), fraction **B-1-3** was collected (Scheme S1-III), which consists of Dy_xSc_{3-x}N@C₇₆ (x=1,2) as the major components (fraction **B-1-3-2**) and Sc₃N@C₈₀ (I) as the contaminant (fraction **B-1-3-1**, removed in the fourth-step isolation by recycling HPLC (Buckyprep column) as shown in Scheme S1-IV). The positive-ion LD-TOF mass spectrum of fraction **B-1-3-2** is shown in Fig. S1, indicating clearly the formation of Dy_xSc_{3-x}N@C₇₆ (x=1,2). The fifth-step isolation by recycling HPLC (Buckyprep-M column, Scheme S1-V) was finally applied aiming to remove Dy₂ScN@C₇₆ (fraction **B-1-3-2-2**) from DySc₂N@C₇₆ (fraction **B-1-3-2-1**).

The relative yield of DySc₂N@C₇₆ (fraction **B-1-3-2-1**) from Dy₂ScN@C₇₆ (fraction **B-1-3-2-2**) is estimated to be 15:1 based on the integrated HPLC peak area (see Scheme S1-V).

Scheme S1. Isolation scheme of DySc₂N@C₇₆. I: The first-step HPLC isolation of a Dy_xSc_{3-x}N@C_{2n} fullerene extract mixture synthesized by the “reactive gas atmosphere” method (linear combination of two 4.6 x 250 mm Buckyprep columns; flow rate 1.6 ml/min; injection volume 100 µl; toluene as eluent (mobile phase); 40°C); II: Chromatogram of the isolated fraction **B** by the second-step recycling HPLC (10 x 250 mm Buckyprep-M column; flow rate 5.0 ml/min; injection volume 5 ml; toluene as eluent; 20°C); III: Chromatogram of the isolated fraction **B-1** by the third-step recycling HPLC (10 x 250 mm Buckyprep column); IV: Chromatogram of the isolated fraction **B-1-3** by the fourth-step recycling HPLC (10 x 250 mm Buckyprep column); V: Chromatogram of the isolated fraction **B-1-3-2** by the fifth-step recycling HPLC (10 x 250 mm Buckyprep-M column). The injection volumes in the 2nd-5th steps are all 5 ml and the flow rate of toluene are kept as 5.0 ml/min. Compositions of fractions are as follow — A: Dy_xSc_{3-x}N@C₇₈ (x=0-3) + Dy_xSc_{3-x}N@C₈₀ (isomer I, x=1, 2); C: Sc₃N@C₈₀ (I) (major); D: Dy_xSc_{3-x}N@C₆₈ (x=0-2); B-2: DySc₂N@C₈₀ (I) + Dy₂ScN@C₈₀ (II); B-3: DySc₂N@C₈₀ (II) + Sc₃N@C₈₀ (I); B-1-1:

DySc₂N@C₈₀ (I); B-1-2: DySc@C₈₄; B-1-3-1: Sc₃N@C₈₀ (I); B-1-3-2-1: DySc₂N@C₇₆; B-1-3-2-2: Dy₂ScN@C₇₆.

Figure S1. Positive-ion LD-TOF mass spectrum of fraction **B-1-3-2**.

S2. Structural analysis of the M_2N ($M=\text{Sc}, \text{Y}$) and YSc_2N clusters within $M_3\text{N}@C_{76}$ and $\text{YSc}_2\text{N}@C_{76}$:

In $\text{Sc}_3\text{N}@C_{76}$, the bond lengths of Sc2-N and Sc2'-N (2.113 Å) is even larger than that found in $\text{Sc}_3\text{N}@C_{80}$ (2.034 Å). In addition, the Sc_3N cluster is slightly pyramidal (the N is 0.083 Å above the Sc_3 plane) (see a, b). In $\text{Y}_3\text{N}@C_{76}$ the corresponding Y-N bond lengths are 2.122 Å (2 times) and 2.072 Å, respectively. The Y_3N cluster is pyramidal with N being 0.256 Å above Y_3 plane (see c). For $\text{YSc}_2\text{N}@C_{76}$ (isomer I), DFT-calculations point out that the YSc_2N cluster is slightly pyramidal in which the N is 0.087 Å above the YSc_2 plane.

Figure S2. DFT-optimized structure of $C_{s:17490}$ $\text{Sc}_3\text{N}@C_{76}$ (a, b), $\text{Y}_3\text{N}@C_{76}$ (c), $\text{YSc}_2\text{N}@C_{76}$ -I (d).

S3. Molecular structural similarity between $C_{76}-C_s:17490$ and $C_{80}(I_h)$ cages:

It is found that $C_{76}-C_s:17490$ cage is genetically close to $C_{80}(I_h)$ cage, i.e. it may be obtained from the latter by removal of four C atoms without a significant rearrangement of the cage.

Figure S3. (a) Schlegel diagram of $C_{80}(I_h)$; (b) atoms and bonds which should be removed (red) and the bonds which should be arranged in $C_{80}(I_h)$ to obtain $C_{76} C_s: 17490$; (c) Schlegel diagram of $C_{76} C_s: 17490$, the adjacent pentagons are shown in bold.

S4. Comparison on the antisymmetric M-N modes in the experimental IR spectrum of $DySc_2N@C_{76}$ and calculated IR spectra of $YSc_2N@C_{76}$ and assignment of the experimental FTIR bands to the calculated frequencies of $YSc_2N@C_{76}(C_s:17490-I)$:

Based on the DFT calculations, the band at 579 cm^{-1} in the spectrum of $DySc_2N@C_{76}$ is assigned to the mixed Dy-N and Sc2-N vibration. This frequency is much lower than Gd-N and Er-N based vibrations in the $GdSc_2N@C_{80}$ and $ErSc_2N@C_{80}$ clusterfullerenes (both 647 cm^{-1}), since the metal-nitrogen bonds in C_{80} -based clusterfullerenes are much shorter than the expected Dy-N and Sc2-N bonds in $DySc_2N@C_{76}$. The band at 660 cm^{-1} is predominantly due to the stretching vibration of the shorter Sc1-N bond. This frequency is close to that of the Sc-N antisymmetric stretching modes in $Sc_3N@C_{68}$ (661 cm^{-1}), and in $ErSc_2N@C_{80}$ (667 cm^{-1}).

Figure S4. FTIR spectrum of $DySc_2N@C_{76}$ (a), calculated IR spectra of $YSc_2N@C_{76}$ based on $C_s:17490-I$ cage isomer (b). The asterisks label the antisymmetric M-N (Sc-N & Dy-N) stretching vibrational modes.

Table S1. Assignment of the experimental FTIR bands to the calculated frequencies of YSc₂N@C₇₆ (C_s:17490-I). As metal atoms are heavy, they do not participate into vibrations of the molecule above 400 cm⁻¹. Hence, vibrational frequencies of DySc₂N@C₇₆ and YSc₂N@C₇₆ are expected to be very close in the experimentally accessible range (>400 cm⁻¹)

calc. freq, cm ⁻¹	calc. int, %	exp.
80.3	3.6	
84.1	2.3	
101.9	14.5	
109.2	6.5	
122.7	8.7	
145.0	7.3	
194.3	1.8	
211.8	1.8	
218.9	0.7	
223.5	0.2	
231.7	13.5	
235.2	0.3	
257.8	0.4	
278.2	0.1	
293.8	0.4	
300.5	0.7	
304.6	0.6	
307.5	0.4	
313.9	0.6	
322.2	0.3	
327.9	0.5	
329.0	0.3	
338.7	0.1	
343.9	0.1	
362.4	0.2	
367.8	0.1	
370.4	1.6	
374.6	0.6	
376.9	0.3	
384.8	2.2	

calc. freq, cm ⁻¹	calc. int, %	exp.
387.2	0.8	
395.3	1.2	
398.7	3.5	
408.5	0.1	
417.1	3.6	
426.9	0.4	
432.6	2.9	
441.5	1.4	
454.7	4.2	
462.1	4.8	467 br, w
466.2	5.6	467 br, w
473.2	2.4	
475.6	1.7	
481.1	15.1	491 vw
491.5	1.6	
497.2	6.8	506 w
498.1	4.8	506 w
503.2	8.4	
504.4	1.0	
510.8	5.0	
514.1	7.0	
518.6	5.0	
521.9	6.2	
525.4	23.3	526 sh
532.0	58.7	539 m
534.2	28.3	539 m
536.3	19.7	539 m
539.5	4.1	
546.3	4.0	
550.9	13.8	578 ms
555.7	24.9	578 ms
561.7	14.3	578 ms
562.7	14.9	578 ms
565.3	3.0	
587.2	2.0	597 w
591.1	0.5	
598.8	0.2	
604.0	0.1	
610.3	0.7	
614.3	1.5	
619.2	3.0	
622.8	2.6	
624.8	1.7	
629.2	1.4	
634.9	1.5	

calc. freq, cm ⁻¹	calc. int, %	exp.
636.6	0.1	
644.6	79.2	660 ms
645.6	6.4	660 ms
649.2	5.9	660 ms
651.5	1.0	
658.2	3.8	
665.5	0.9	
669.4	2.5	
677.9	3.8	692 w
680.2	1.9	692 w
681.9	3.5	692 w
684.1	0.3	
686.2	0.7	
689.6	3.1	
691.6	1.4	
696.1	0.7	
699.9	1.2	
703.2	5.3	714 w
704.9	2.3	714 w
706.6	1.0	714 w
708.1	4.8	714 w
711.9	1.1	
713.0	0.7	
719.0	0.1	
721.4	0.5	
725.1	1.8	
727.3	0.3	
729.0	0.1	
734.3	0.2	
738.2	0.4	
739.8	0.7	
744.0	2.2	
745.2	0.8	
747.3	0.2	
750.4	2.8	761 w
751.5	3.2	761 w
754.3	2.1	
761.8	0.8	
764.0	4.0	
770.0	1.8	
773.1	2.4	
774.1	2.2	
777.7	5.3	807 m
778.1	0.9	
781.4	0.6	

calc. freq, cm ⁻¹	calc. int, %	exp.
784.4	1.1	
791.3	0.3	
800.7	0.9	
818.3	0.1	
830.7	1.2	
840.1	1.0	
864.4	0.4	
869.9	5.0	875 w
872.4	0.6	
876.5	1.3	
880.0	1.4	
882.3	1.8	
889.3	10.1	886 w
899.5	0.5	
903.7	2.3	898 w
907.3	1.3	898 w
1009.9	5.6	1012 br,w
1015.4	0.4	
1023.2	6.6	
1027.0	6.2	1012 br,w
1035.6	3.1	
1038.4	2.2	
1044.3	3.5	1050 m
1045.4	12.9	1050 m
1047.3	2.0	
1105.0	19.4	1113 m
1111.1	4.7	
1119.5	3.0	
1128.0	6.1	
1133.7	0.8	
1137.4	6.5	1142 w
1147.2	5.1	1142 w
1151.6	0.6	
1157.9	0.4	
1167.8	0.6	
1170.2	0.5	
1173.7	0.4	
1177.5	2.5	
1188.0	14.2	1195 w
1190.3	4.9	
1195.8	4.2	
1201.2	1.3	
1209.5	12.4	1218 w
1216.3	4.5	
1227.8	4.6	

calc. freq, cm ⁻¹	calc. int, %	exp.
1233.1	2.0	
1236.3	2.6	
1241.8	6.9	
1247.3	3.3	
1249.7	2.4	
1254.0	2.7	
1257.3	15.6	1271 m
1260.4	14.2	1271 m
1261.0	19.3	1271 m
1270.7	7.8	
1272.1	3.6	
1276.0	1.5	
1279.0	0.7	
1283.5	15.1	1297 w
1289.8	9.5	
1294.6	5.2	
1302.7	9.4	
1310.0	9.2	
1318.5	3.6	
1322.1	20.4	1334 ms, sh
1324.2	39.3	1334 ms, sh
1331.8	28.1	1334 ms, sh
1335.8	18.2	
1337.0	25.3	
1339.9	3.1	
1344.2	43.9	1354 s, sh
1346.0	21.7	1354 s, sh
1348.0	51.5	1354 s, sh
1353.8	59.4	1371 vs
1359.0	100.0	1371 vs
1360.4	46.3	1371 vs
1361.5	12.6	
1365.5	64.9	1371 vs
1369.4	9.5	
1370.3	4.8	
1374.3	31.4	1381 vs, sh
1379.3	42.3	1381 vs, sh
1385.0	1.5	
1393.2	18.8	1410 w
1398.7	9.9	
1401.9	4.2	
1404.3	4.9	
1412.5	7.6	
1414.1	2.2	
1415.6	0.2	

calc. freq, cm ⁻¹	calc. int, %	exp.
1418.0	4.3	
1422.5	4.4	
1424.5	9.2	1442 w
1432.3	4.7	
1436.1	6.0	1451 w
1437.6	2.0	
1445.9	0.4	
1446.6	9.8	1463 w
1453.6	9.1	1463 w
1455.6	5.2	
1461.7	2.4	
1471.2	0.7	
1474.2	1.3	
1476.7	3.1	
1480.5	1.1	
1485.5	40.7	1501 m
1487.4	8.3	
1492.5	3.9	
1494.6	0.9	
1503.0	1.4	
1506.1	8.0	1534 w
1509.5	2.6	
1512.6	2.8	
1524.8	4.7	1550 w

vw - very weak, w – weak, m – medium,
ms – medium strong, s – strong, sh –
shoulder, br – broad

S5. Comparison of the computed IR spectra of selected most stable isomers of YSc₂N@C₇₆ to the experimental spectrum of DySc₂N@C₇₆:

Figure S5. FTIR spectrum of DySc₂N@C₇₆ in comparison with the computed IR spectra of several selected most stable isomers of YSc₂N@C₇₆.