Supporting Information

Endohedral Metal or a Fullerene Cage Based Oxidation? Redox Duality of Nitride Clusterfullerenes $Ce_xM_{3-x}N@C_{78-88}$ (x = 1, 2; M = Sc and Y) Dictated by the Scaffold Metals and the Carbon Cage Size

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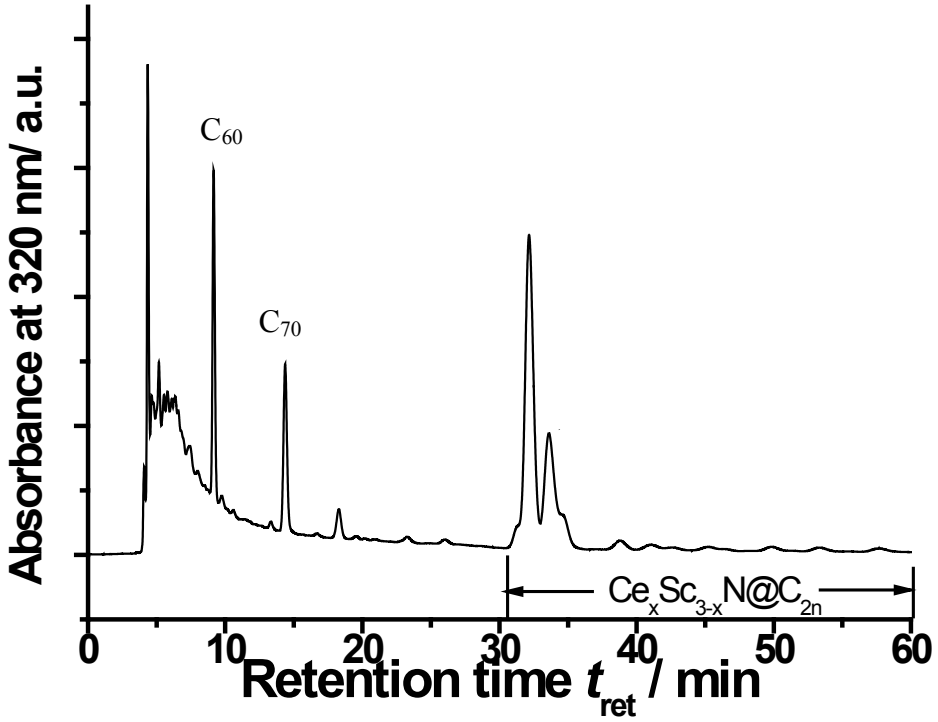
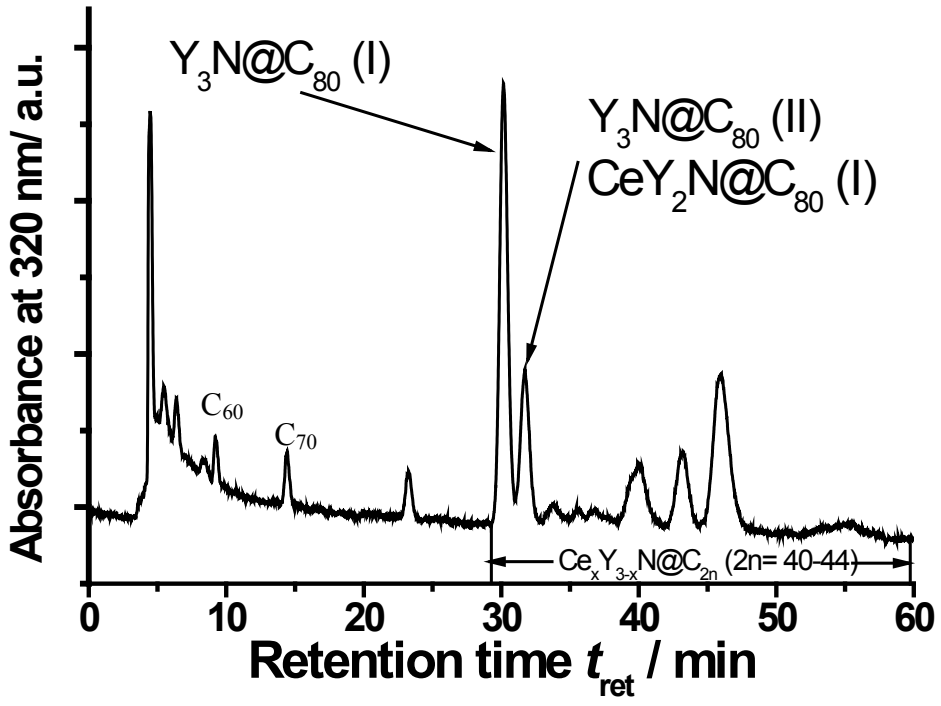
HPLC traces of Ce-Sc and Ce-Y extracts





HPLC Separation of $Ce_xY_{3-x}N@C_{2n}$ NCFs

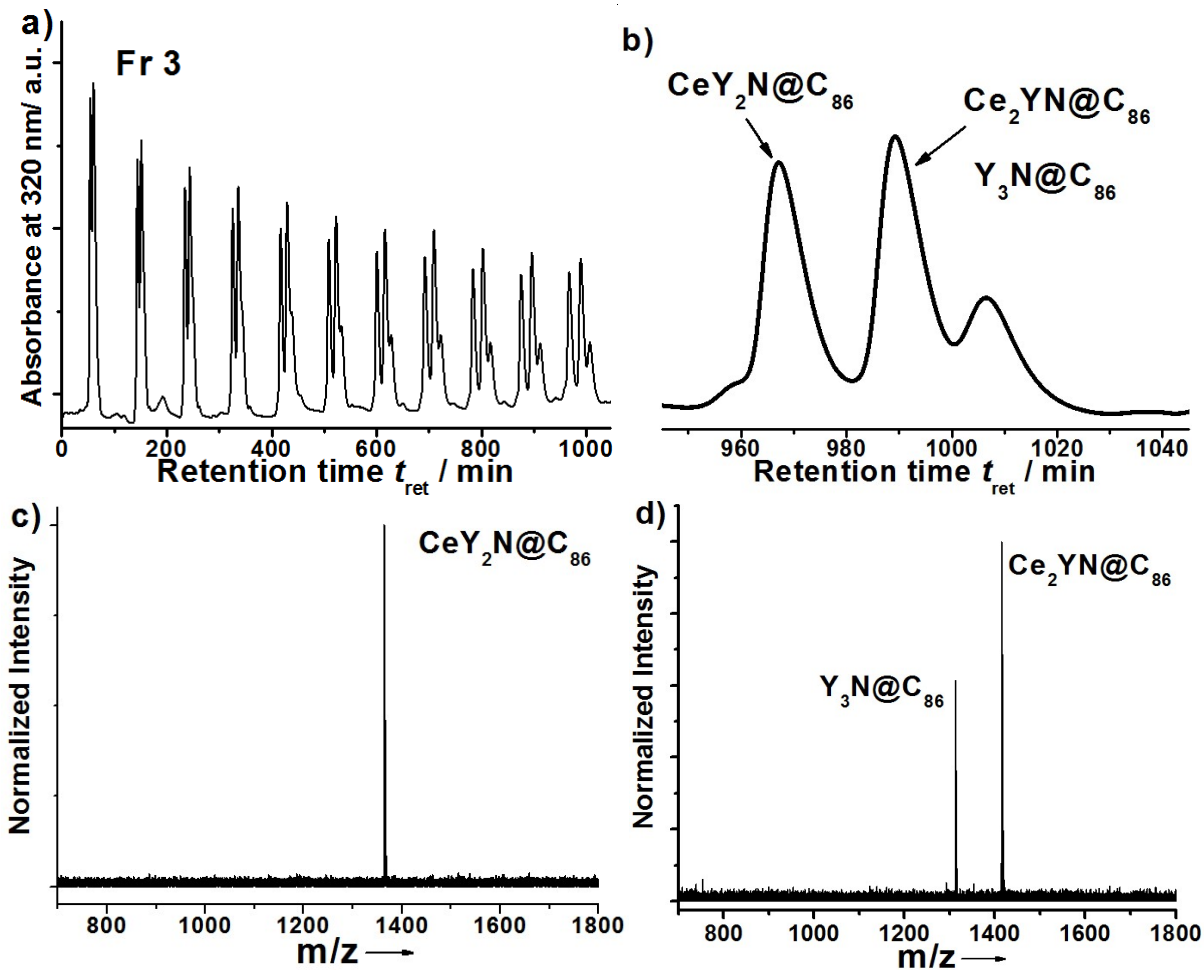


Figure S1. Chromatogram of the Fraction 3 of $Ce_xY_{3-x}N@C_{86}$ fullerenes extract mixture synthesized by the "SOS" method (10×250 mm Buckyprep column, flow rate was set at 2.0 ml/min, injection volume 3 mL, toluene as mobile phase, room temperature). (a) several cycles of recycling HPLC; (b) enlarged view on the HPLC profile after 11 cycles showing individual components; (c) mass-spectra of purified $CeY_2N@C_{86}$ and inseparable mixture of $Y_3N@C_{86}$ and $Ce_2YN@C_{86}$

$CeY_2N@C_{86}$ was obtained by running recycling HPLC with Fraction 3. Because the retention time of $Y_3N@C_{86}$ and $Ce_2YN@C_{86}$ is close, this sub-fraction was collected as the mixture of these two structures.

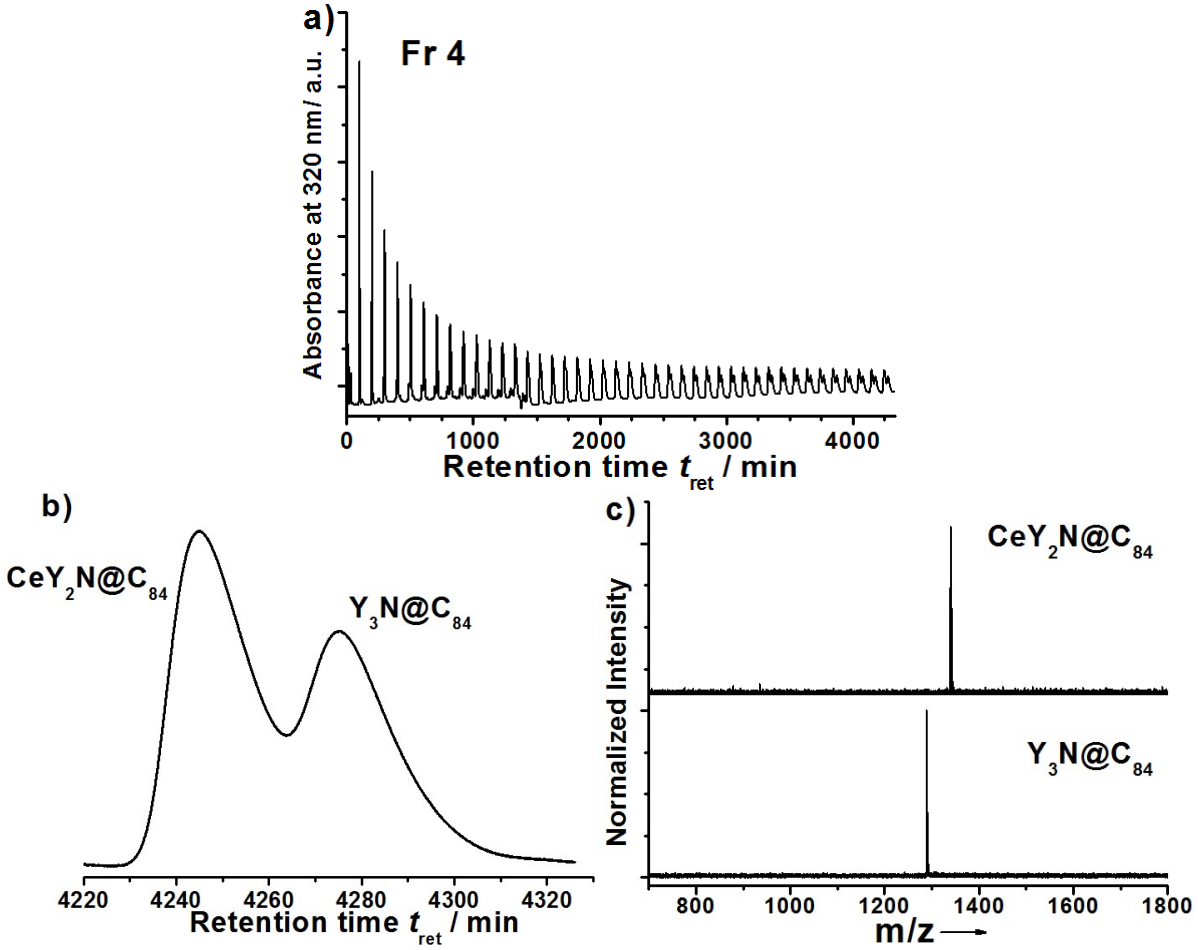


Figure S2. Chromatogram of the Fraction 4 of $Ce_xY_{3-x}N@C_{84}$ fullerenes extract mixture synthesized by the "SOS" method (10×250 mm Buckyprep column, flow rate 2.0 ml/min, injection volume 3 mL, toluene as mobile phase, room temperature). (a) 42 cycles of recycling HPLC; (b) enlarged view on the HPLC profile after 42 cycles showing individual components; (c) mass-spectra of purified $Y_3N@C_{84}$ and $CeY_2N@C_{84}$

$CeY_2N@C_{84}$ and $Y_3N@C_{84}$ are major structures in the Fraction 4. Both of them were isolated after 42 cycles. Confirmation of their purity was performed by LDI-TOF mass spectroscopy that confirmed theirs high purity.

HPLC Separation of $Ce_xSc_{3-x}N@C_{2n}$ NCFs

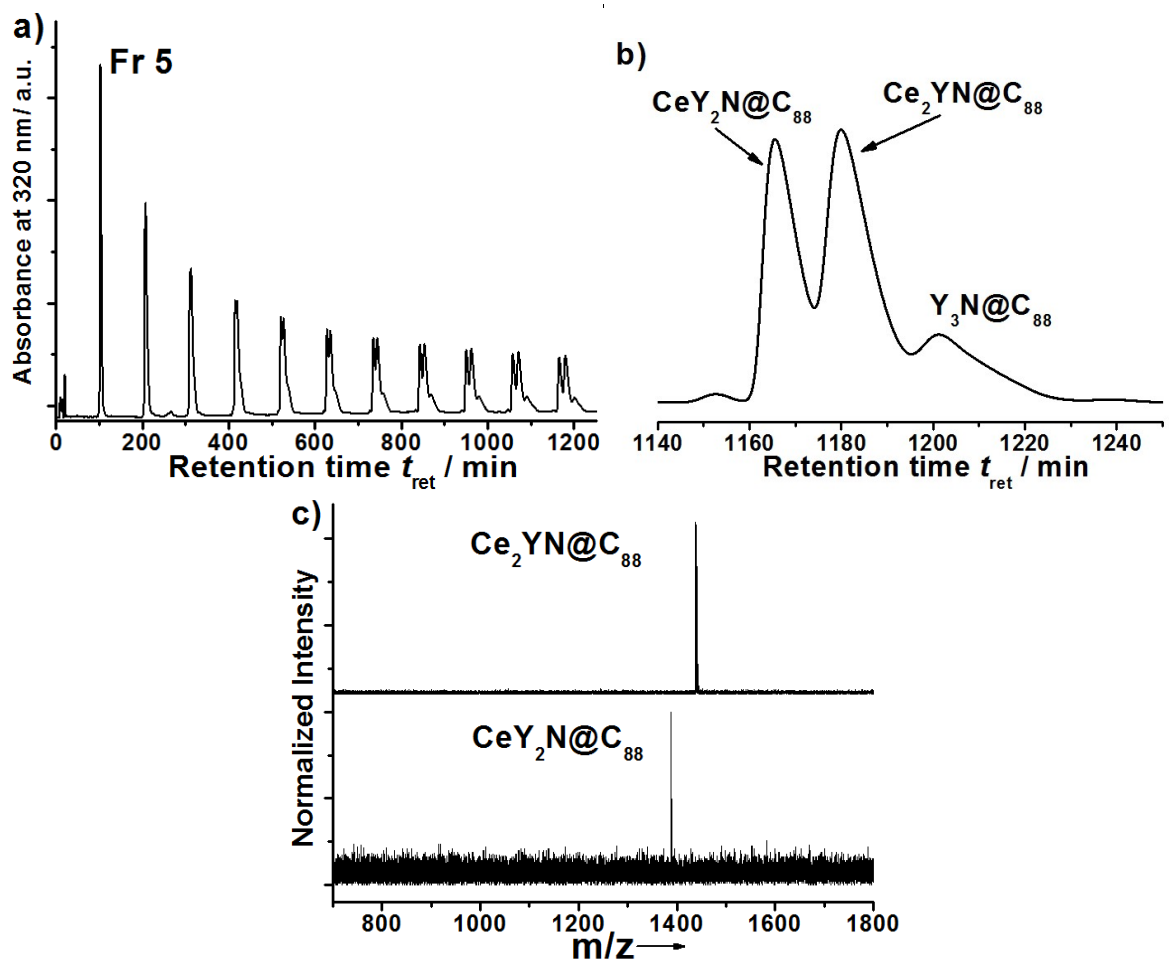


Figure S3. Chromatogram of the Fraction 5 of $Ce_xY_{3-x}N@C_{88}$ fullerenes extract mixture synthesized by the "SOS" method (10×250 mm Buckyprep column, flow rate 2.0 ml/min, injection volume 3 mL, toluene as mobile phase, room temperature): (a) several cycles of recycling HPLC; (b) enlarged view on the HPLC profile after 11 cycles showing individual components; (c) mass-spectra of purified $Ce_2YN@C_{88}$ and $CeY_2N@C_{88}$

In Fraction 5, $Ce_2YN@C_{88}$ and $CeY_2N@C_{88}$ were isolated after 11 cycles. Confirmation of their purity was performed by LDI-TOF mass spectroscopy.

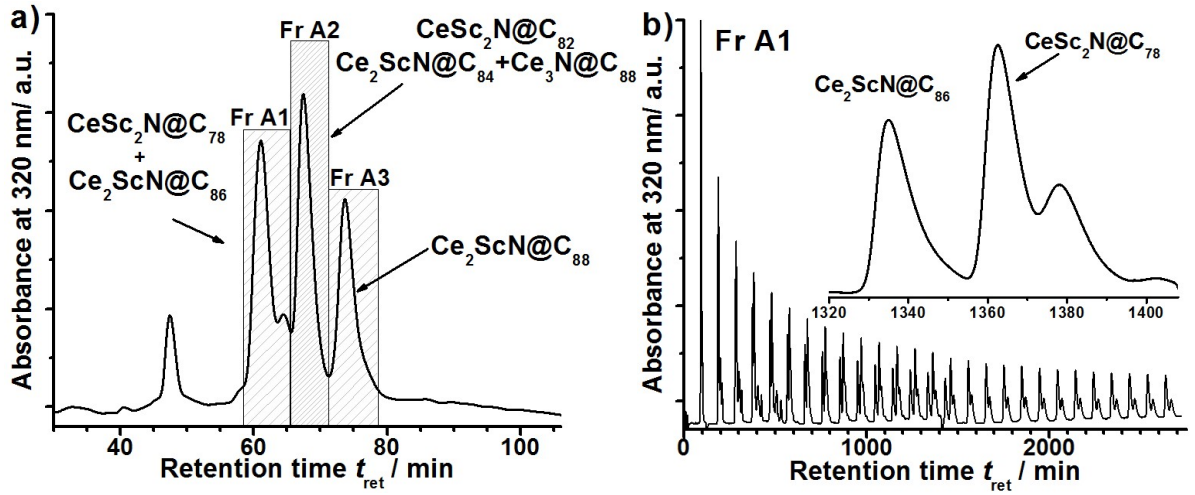


Figure S4. Chromatogram of the Fraction A of $Ce_xSc_{3-x}N@C_{2n}$ fullerenes extract mixture synthesized by the "SOS" method (10×250 mm Buckyprep column, flow rate was set at 3.0 ml/min, injection volume 3 mL, toluene as mobile phase, room temperature): (a) the first cycle of recycling HPLC; (b) recycling HPLC of fraction A1 and enlarged view on the HPLC profile after 15 cycles showing individual components;

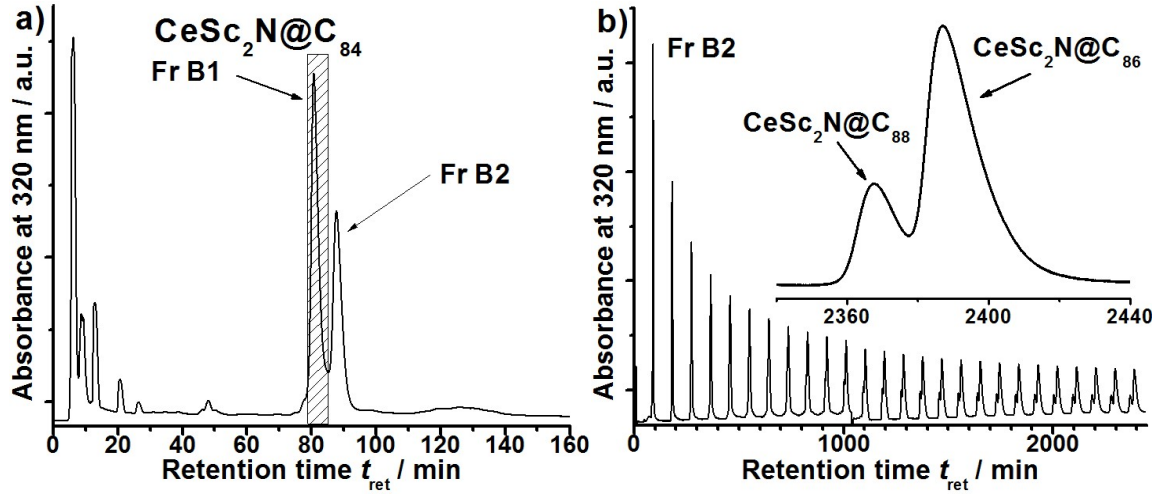


Figure S5. Chromatogram of the Fraction B of $CeSc_2N@C_{84,\ 86,\ 88}$ fullerenes extract mixture synthesized by the "SOS" method (10×250 mm Buckyprep column, flow rate was set at 3.0 ml/min, injection volume 3 mL, toluene as mobile phase, room temperature).): (a) the first cycle of recycling HPLC; (b) recycling HPLC of fraction B2 and enlarged view on the HPLC profile after 26 cycles showing individual components

As shown in Fig 1, fraction A (t_{ret}= 40.0-52.0 min) and fraction B (t_{ret}= 52.0-59.0 min) of Ce/Sc MMNCFs were collected for the second-step seperation which contains $CeSc_2N@C_{2n}$ structures. At the second step, a 10×250 mm Buckyprep column was used to separate fraction A into three sub-fractions, namely fraction A1, A2 and A3. The $Ce_2ScN@C_{88}$ was isolated from fraction A3. The fraction A1 was injected to recycling HPLC for further isolation. $Ce_2ScN@C_{86}$ and $CeSc_2N@C_{78}$ were isolated after 15 and 27 cycles respectively. The same

Buckyprep column (10×250 mm) was used to separate fraction B into two sub-fractions, fraction B1 and B2. $CeSc_2N@C_{84}$ was isolated from fraction B1. Because the retention time of $CeSc_2N@C_{88}$ and $CeSc_2N@C_{86}$ in fraction B2 is close, these two structures were collected by running recycling HPLC after 26 cycles.

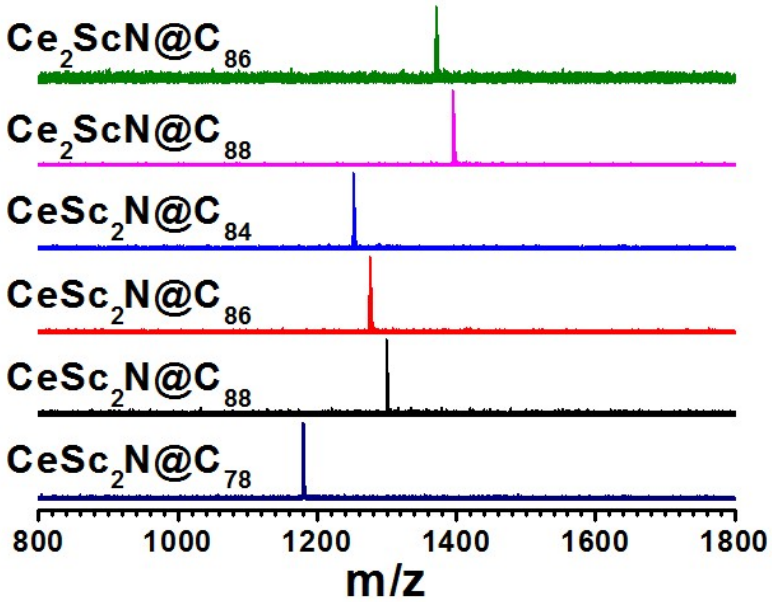


Figure S6. The LDI-TOF mass spectra of $Ce_xSc_{3-x}N@C_{2n}$ (2n= 78-88).

Table S1. Redox potential of $Ce_xM_{3-x}N@C_{2n}$ (M= Sc, Y; 2n= 78-88) determined by cyclic voltammetry (CV) and square-wave voltammetry (SW). All values are in V versus $Fe(Cp)_2^{+/0}$ couple; [] - peak potentials for irreversible steps (in CV).

		ox-II	ox-I	red-I	red-II	red-III	gap_{EC}
$CeSc_2N@C_{78}$	CV	0.94	0.18	[−1.37]	[−1.84]		1.55
	SW	0.95	0.18	−1.32	−1.79		1.50
$GdSc_2N@C_{78}$	CV	[0.92]	0.45	[−1.44]	[−1.88]		1.89
	SW	0.84	0.46	−1.38	−1.86		1.84
$CeY_2N@C_{80}$	CV		−0.07	[−1.36]	[−1.88]		1.30
	SW		−0.06	−1.32	−1.83		1.25
$CeLu_2N@C_{80}$	CV		0.01	[−1.43]	[−1.92]		1.44
	SW		0.01	−1.39	−1.88		1.40
$CeSc_2N@C_{80}$	CV		0.33	[−1.34]	[−1.87]		1.67
	SW	1.11	0.33	−1.31	−1.83		1.64
$PrSc_2N@C_{80}$	CV		0.64	[−1.32]	[−1.91]		1.96
	SW	1.11	0.64	−1.26	−1.83		1.91
$Y_3N@C_{84}$	CV	0.75	0.34	[−1.35]	[−1.78]		1.69
	SW	0.75	0.34	−1.30	−1.73		1.64
$CeY_2N@C_{84}$	CV	0.81	0.22	[−1.36]	[−1.81]		1.58
	SW	0.82	0.23	−1.29	−1.75		1.52
$CeLu_2N@C_{84}$	CV	[0.83]	0.31	[−1.43]	[−1.89]		1.74
	SW	0.77	0.31	−1.39	−1.84		1.70
$CeSc_2N@C_{84}$	CV	0.77	0.37	[−1.31]	[−1.77]	[−2.38]	1.68
	SW	0.78	0.37	−1.26	−1.73	−2.33	1.63
$Y_3N@C_{88}$	CV	0.50	0.10	−1.30	−1.64	−2.13	1.40
	SW	0.51	0.10	−1.29	−1.62/−1.83	−2.12	1.39
$CeY_2N@C_{88}$	CV	0.53	0.10	−1.29	[−1.62/−1.70]	−2.12	1.39
	SW	0.53	0.10	−1.28	−1.60	−2.12	1.38
$Ce_2YN@C_{88}$	CV	0.55	0.13	−1.25	−1.61	−2.12	1.38
	SW	0.55	0.13	−1.25	−1.62	−2.12	1.37
$CeSc_2N@C_{88}$	CV	[0.45]	0.03	[−1.22]	−1.71		1.25
	SW	0.41	0.04	−1.16	−1.71		1.20
$Ce_2ScN@C_{88}$	CV	0.51	0.10	−1.22	−		1.31
	SW	0.51	0.09	−1.22	−1.75		1.31
$Gd_2ScN@C_{88}$	CV	0.48	0.07	−1.26	−1.63	−2.05	1.33
	SW	0.49	0.08	−1.26	−1.63	−2.05	1.34
$Y_3N@C_{86}$	CV	0.77	0.36	[−1.33]	[−1.73]		1.69
	SW	0.78	0.36	−1.28	−1.68		1.65
$CeY_2N@C_{86}$	CV	0.82	0.27	[−1.38]	[−1.76]	−	1.65
	SW	0.83	0.27	−1.34	−1.73		1.61
$Ce_2YN@C_{86}$	CV		0.17	[−1.35]	[−1.75]		1.52
	SW		0.16	−1.32	−1.71		1.48
$Ce_2ScN@C_{86}$	CV	0.76	0.29	[−1.24]	[−1.71]	[−2.22]	1.53
	SW	0.77	0.29	−1.20	−1.65	−2.21	1.49
$CeSc_2N@C_{86}$	CV	[0.80]	0.34	[−1.39]	[−1.77]	[−2.28]	1.73
	SW	0.75	0.34	−1.32	−1.71	−2.21	1.66

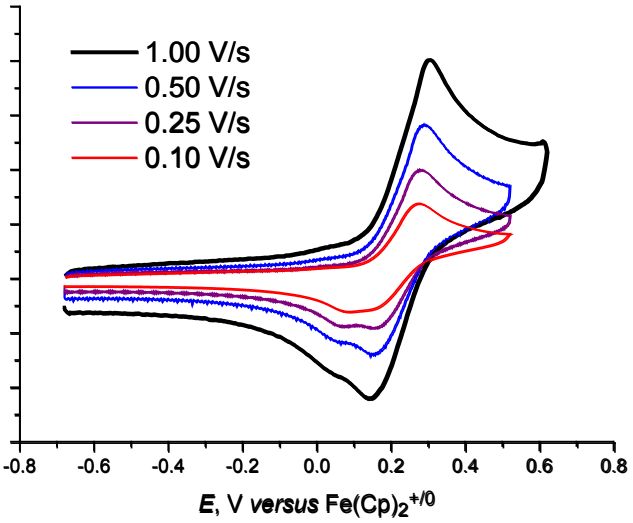


Figure S7. The first oxidation of $CeY_2N@C_{84}$ measured at different scan rates

Table S2. Difference between IP_{cage} and IP_{Ce} computed with different density functionals

DFT Functional	$\Delta IP = IP_{Ce} - IP_{cage}$
SOGGAX	+0.19
SOGGA	−1.04
O3LYP	−0.50
PBE-0X (aka PBE)	−0.67
PBE-05X	−0.56
PBE-10X	−0.50
PBE-15X	−0.31
PBE-20X	−0.23
PBE-25X (aka PBE0)	−0.11
experimental $\Delta E_{1/2}$	−0.31

coordinates were optimized at the PBE0 level; PBE-YYX denotes PBE functional with YY% of exact exchange term (PBE-0X is pure GGA functional, PBE-25X is known as PBE0); "experimental" value is a difference of the first oxidation potentials of $CeSc_2N@C_{80}$ and $PrSc_2N@C_{80}$.