**Supporting Information for:** 

# Entrapping a Group-VB Transition Metal, Vanadium, within an Endohedral Metallofullerene: V<sub>x</sub>Sc<sub>3-x</sub>N@*I*<sub>b</sub>-C<sub>80</sub> (x=1, 2)

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**Figure S1.** (I) Chromatograms of the fullerene extract mixtures obtained from VC with N<sub>2</sub> addition (VC/N<sub>2</sub>, a), pure VC (b), pure V<sub>2</sub>O<sub>5</sub> (c) and pure graphite (empty-C, d). (II) Chromatograms of the fullerene extract mixtures obtained from VC/Sc<sub>2</sub>O<sub>3</sub> with N<sub>2</sub> addition (VC/Sc<sub>2</sub>O<sub>3</sub>/N<sub>2</sub>, e), V<sub>2</sub>O<sub>5</sub>/Sc<sub>2</sub>O<sub>3</sub> with N<sub>2</sub> addition (V<sub>2</sub>O<sub>5</sub>/Sc<sub>2</sub>O<sub>3</sub>/N<sub>2</sub>, f), Sc<sub>2</sub>O<sub>3</sub> with N<sub>2</sub> addition (Sc<sub>2</sub>O<sub>3</sub>/N<sub>2</sub>, g), VC with N<sub>2</sub> addition (VC/N<sub>2</sub>, h). (20 × 250 mm Buckyprep column; flow rate: 15 mL•min<sup>-1</sup>; injection volume: 15 mL; toluene as eluent; 40 °C). **B** (**B**'): Sc<sub>3</sub>N@C<sub>80</sub> (*I<sub>h</sub>+D<sub>5h</sub>*) + C<sub>86</sub>.

#### S2. LD-TOF mass spectra of extract mixtures obtained under different conditions.



**Figure S2.** Positive-ion laser desorption time-of-flight (LD-TOF) mass spectra of the fullerene extract mixtures obtained from pure  $V_2O_5$  (a),  $V_2O_5$  with  $N_2$  addition ( $V_2O_5/N_2$ , b), VC with  $N_2$  addition (VC/N<sub>2</sub>, c) and pure VC (d). The inset show the enlarged region of m/z=1050-1160.

# S3. LD-TOF mass spectra of fractions A, A1 and A2.



**Figure S3.** (left) Positive-ion laser desorption time-of-flight (LD-TOF) mass spectra of fraction **A** isolated from VC/Sc<sub>2</sub>O<sub>3</sub>/N<sub>2</sub> extract and the isolated sub-fractions **A1** and **A2**. The spectrum of fraction A' isolated from Sc<sub>2</sub>O<sub>3</sub>/N<sub>2</sub> extract is also shown for comparison. (right) The enlarged region of m/z=1050-1130.

# S4. Isolation of $V_x Sc_{3-x} N@I_h(7)-C_{80}(x=1, 2)$ and estimation of their relative yield.



1) Isolation of  $V_x Sc_{3-x} N@I_h(7)-C_{80}(x=1, 2)$ :

**Figure S4.** (I) Recycling HPLC chromatogram of fraction **A** isolated from VC/Sc<sub>2</sub>O<sub>3</sub>/ N<sub>2</sub> extract (10 × 250 mm Buckyprep-M column; flow rate 5 ml/min; injection volume 5 ml; toluene as eluent; 40 °C). **A-1:** C<sub>90</sub>+Sc<sub>2</sub>C<sub>82</sub>+Sc<sub>2</sub>C<sub>84</sub>, **A-2:** Sc<sub>2</sub>C<sub>84</sub>, **A-3:** V<sub>x</sub>Sc<sub>3-x</sub>N@C<sub>80</sub> (x=1, 2). (II) Recycling HPLC chromatogram of sub-fraction **A-3** (10 × 250 mm Buckyprep column; flow rate 5 ml/min; injection volume 5 ml; toluene as eluent; 40 °C). **A-3-1:** V<sub>2</sub>ScN@C<sub>80</sub>, **A-3-2:** VSc<sub>2</sub>N@C<sub>80</sub>. Inset: Enlarged chromatographic region of 1414 – 1475 min.

 $V_xSc_{3-x}N@I_h(7)-C_{80}$  (x=1, 2) were isolated by three-step HPLC. In the first step, the fullerene extract mixture was isolated by a 20 × 250 mm Buckyprep column, and fraction **A** with retention time ranging from 46.9 to 49.9 min was collected (see Fig. S1II). In the second-step isolation, the collected fraction **A** was subjected to the recycling HPLC isolation running in a 10 × 250 mm Buckyprep-M column, and sub-fraction **A-3** was collected after two cycles (see Fig. S4(I)). In the third step, the collected sub-fraction **A-3** was further isolated by recycling HPLC using a 10 × 250 mm Buckyprep column, resulting in isolation of fractions **A-3-1** and **A-3-2** after 87

recycles corresponding to  $V_2$ ScN@C<sub>80</sub> and VSc<sub>2</sub>N@C<sub>80</sub>, respectively, which were further checked by LD-TOF MS measurement as shown in Figure 1. In order to avoid overlapping of the two shoulder peaks during long time recycling process, we constantly collected the latter peak by cutting it from near half peak height intensity after 42 recycles (see inset of Fig. S4(II)).

#### 2) Estimation of the relative yield of $V_x Sc_{3-x} N@I_h(7)-C_{80}(x=1, 2)$ :

The relative yield of  $V_2$ ScN@ $I_h(7)$ -C<sub>80</sub> and VSc<sub>2</sub>N@ $I_h(7)$ -C<sub>80</sub> to Sc<sub>3</sub>N@ $I_h(7)$ -C<sub>80</sub> is estimated based on the integration area of the corresponding peaks in the chromatograms shown in curve e of Figs. S1II and S4.

Fraction	Sub-fraction	Major component	Relative
			abundance
В	-	$Sc_3N@I_h(7)-C_{80}$	67.2%
		$Sc_3N@D_{5h}(6)-C_{80}$	28.6%
		$C_{86}$	4.2%
Α	A-1 + A-2	C <sub>90</sub> , Sc <sub>2</sub> C <sub>82</sub> , Sc <sub>2</sub> C <sub>84</sub>	93.2%
	A-3	$V_2$ ScN@ $I_h(7)$ -C <sub>80</sub> ,	6.8%
		$\mathrm{VSc}_{2}\mathrm{N}@I_{h}(7)-\mathrm{C}_{80}$	
A-3	A-3-1	$V_2 Sc N@I_h(7)-C_{80}$	12.8%
	A-3-2	$VSc_2N@I_h(7)-C_{80}$	87.2%

**Table S1.** Assignments of each (sub)fraction and their relative abundance.

Accordingly the relative yield of  $V_2$ ScN@ $I_h(7)$ -C<sub>80</sub> to VSc<sub>2</sub>N@ $I_h(7)$ -C<sub>80</sub> can be calculated as:

 $V_2$ ScN@ $I_h(7)$ -C<sub>80</sub>: VSc<sub>2</sub>N@ $I_h(7)$ -C<sub>80</sub> = 12.8% : 87.2%  $\approx$  1:6.8

Given that relative yield of fraction **A**:**B** is ~1:4, the relative yield of  $V_2ScN@I_h(7)-C_{80}$  to  $Sc_3N@I_h(7)-C_{80}$  can be calculated as:

$$V_2$$
ScN@ $I_h(7)$ -C<sub>80</sub> : Sc<sub>3</sub>N@ $I_h(7)$ -C<sub>80</sub> = 12.8% × 6.8% : (67.2% × 4) ≈ 1: 308.8



Figure S5. Positive-ion laser desorption time-of-flight (LD-TOF) mass spectrum of fraction A-3.

In the process of MS characterization of  $V_xSc_{3-x}N@C_{80}$  (x=1, 2), we observed an intense mass peak of m/z=1113 overlapping with the signal of 1115 (VSc<sub>2</sub>N@C<sub>80</sub>) in fraction **A-3** (see Fig. S5), corresponding to a chemical form of  $V_3C_{80}$  which might be a trimetallofullerene  $V_3@C_{80}$  or metal carbide clusterfullerene  $V_3C_2@C_{78}$ .<sup>[S1-S3]</sup> In order to isolate  $V_3C_{80}$ , we carried out recycling HPLC isolation of fraction **A-3** using a Buckyprep column. However, unfortunately there were only two peaks corresponding to  $V_2ScN@C_{80}$  and  $VSc_2N@C_{80}$  even after recycling 87 times (see Fig. S4), thus our initial attempt to isolate  $V_3C_{80}$  was unsuccessful. A possible reason is, like the reported  $Y_3@C_{80}$ ,<sup>[S3]</sup> although  $V_3C_{80}$  exhibits an intense MS peak at m/z=1113 even comparable to that of m/z=1121 ( $V_2ScN@C_{80}$ ), this is mainly because of its small ionization potential but its actual yield is extremely low. Besides, we also carefully checked the existence of other possible V-containing EMFs such as monometallofullerenes ( $V@C_{2n}$ ) and dimetallofullerenes ( $V_2C_{2n}$ ) in both the extract mixture and isolated fractions based on MS measurements, but did not find these compounds probably because of their extremely low yields below our detection limit.

## S6. X-ray crystallographic analysis of $V_x Sc_{3-x} N@I_h(7)-C_{80} (x=1, 2)$ .

# 1) $VSc_2N@I_h(7)-C_{80}$ :

The cocrystal of VSc<sub>2</sub>N@C<sub>80</sub>·Ni<sup>II</sup>(OEP)·1.67C<sub>6</sub>H<sub>6</sub>·0.33CHCl<sub>3</sub> is monoclinic with a space group of C2/m. Thus, its asymmetric unit cell contains a half of the Ni<sup>II</sup>(OEP) molecule and a half of VSc<sub>2</sub>N@C<sub>80</sub> molecule. Although the Ni<sup>II</sup>(OEP) molecule is fully ordered, the  $I_h(7)$ -C<sub>80</sub> carbon cage and the internal VSc<sub>2</sub>N cluster are disordered for VSc<sub>2</sub>N@ $I_h(7)$ -C<sub>80</sub>. There are three orientations for the  $I_h(7)$ -C<sub>80</sub> carbon cage, and the major orientation of the  $I_h(7)$ -C<sub>80</sub> cage with an occupancy of 0.409 is formed by the existed half combining with its mirror image since one of  $I_h(7)$ -C<sub>80</sub> symmetry planes coincides with the crystallographic mirror plane (see Fig. 2A). For the other two minor orientations of  $I_h(7)$ -C<sub>80</sub> cage, since there is no any symmetry plane of the  $I_h(7)$ -C<sub>80</sub> cage coincident with the crystallographic mirror plane, the intact  $I_h(7)$ -C<sub>80</sub> cage is formed by combining one of the halves of the carbon cage with the mirror image of the other. Accordingly, these two minor orientations share the same occupancy of 0.295. For the major orientation of the  $I_h(7)$ -C<sub>80</sub> cage, the shortest distance between the carbon cage involving C33 and nickel ion in Ni<sup>II</sup>(OEP) is 2.94(8) Å, larger than those reported for cocrystals of MSc<sub>2</sub>N@C<sub>80</sub> (M=La, Ce, Gd, Tb) with Ni<sup>II</sup>(OEP).<sup>[S4-S6]</sup>

Within the  $I_h(7)$ -C<sub>80</sub> cage, the entrapped VSc<sub>2</sub>N cluster shows two disorders with occupancy of 0.601 and 0.399, respectively, while the central N atom located at the center of the cavity and on the mirror plane of the entire molecule as well is fully ordered. This case is obviously different from those of lanthanide metal-based MMNCFs MSc<sub>2</sub>N@ $I_h(7)$ -C<sub>80</sub> (M=Er, Tb) which have even nearly four disorders for the whole inner cluster<sup>[S4,S7]</sup>. The major site of VSc<sub>2</sub>N cluster is comprised of V1 with an occupancy of 0.342, Sc1 with an occupancy of 0.601 and Sc1a with an equal occupancy as the mirror image of Sc1, whereas the minor VSc<sub>2</sub>N cluster contains V2, Sc2 and Sc2a with occupancy of 0.658, 0.399, and 0.399, respectively (see Fig. S5A for its relative orientation to the major VSc<sub>2</sub>N site).

#### 2) $V_2ScN@I_h(7)-C_{80}$ :

Similar to the case of  $VSc_2N@I_h(7)-C_{80}$ , the cocrystal of  $V_2$ ScN@C<sub>80</sub>·Ni<sup>II</sup>(OEP)·2C<sub>6</sub>H<sub>6</sub> is also monoclinic with a space group of C2/m. Accordingly, its asymmetric unit cell contains a half of the Ni<sup>II</sup>(OEP) molecule (which is fully ordered) and a half of  $V_2ScN@C_{80}$  molecule.  $V_2ScN@I_h(7)$ -C<sub>80</sub> also exhibits disordering for the  $I_h(7)$ -C<sub>80</sub> carbon cage and the internal V<sub>2</sub>ScN cluster. Although three orientations for the  $I_h(7)$ -C<sub>80</sub> carbon cage of V<sub>2</sub>ScN@ $I_h(7)$ -C<sub>80</sub> are also refined, the minor orientation of the  $I_h(7)$ -C<sub>80</sub> cage with an occupancy of 0.248, similar to the case of  $VSc_2N@I_h(7)$ -C<sub>80</sub>, is obtained by the existed half combining with itself mirror image, while the other two major orientations of the  $I_h(7)$ -C<sub>80</sub> cage with an equal occupancy of 0.376 were finally obtained by combining one of the halves of the fullerene cage with the mirror image of the other (see Fig. 2B). For the major orientation of the  $I_h(7)$ -C<sub>80</sub> cage, the shortest cage-Ni contact involves C56 with a distance of 2.82 (1) Å, which is much smaller than that for  $VSc_2N@C_{80}$ (2.94(8) Å) but resembles to those reported for cocrystals based on MSc<sub>2</sub>N@C<sub>80</sub> (M=La, Ce, Gd, Tb) MMNCFs.<sup>[S4-S6]</sup>.

Like VSc<sub>2</sub>N@ $I_h(7)$ -C<sub>80</sub>, there are also two disorders for the entrapped V<sub>2</sub>ScN cluster within V<sub>2</sub>ScN@ $I_h(7)$ -C<sub>80</sub>. However, apparently different to the case of VSc<sub>2</sub>N@ $I_h(7)$ -C<sub>80</sub>, the two sites of the entrapped V<sub>2</sub>ScN cluster share the same occupancy. One site is comprised of Sc1 (with 0.50 fractional occupancy), V1 (with 0.577 fractional occupancy) and V2a (with 0.423 fractional occupancy) and, coincidentally, the other site is based on the mirror image of the first one (see Fig. S5B for the relative orientations of these two sites).



**Figure S6.** (A) Drawing showing the relative positions of two VSc<sub>2</sub>N sites inside the  $I_h(7)$ -C<sub>80</sub> cage, including the major one composed of (Sc1, Sc1a, V1) and the minor one consisting of (Sc2, Sc2a, V2). (B) Drawing showing the relative positions of two V<sub>2</sub>ScN sites inside the  $I_h(7)$ -C<sub>80</sub> cage, including one site composed of (Sc1, V1, V2a) and the other site consisting of (Sc1a, V1a, V2). All atoms are shown in 30% thermal ellipsoids. C, N, Sc and V atoms are shown in gray, blue, green and red, respectively. A crystallographic mirror plane is aligned vertically across the center of the molecule (along the dash line and perpendicular to the page), coincident with one symmetric plane of  $I_h(7)$ -C<sub>80</sub>.

**Table S2.** Crystal and structure data of  $VSc_2N@I_h(7)-C_{80}$  at 100 K.

Temperature	T = 100 K	Crystal size	$0.22 \times 0.17 \times 0.15 \text{ mm}^3$
Empirical formula	C126 H54 Cl N4 Ni Sc2 V	Reflections collected	7195
Formula weight	1865.26	Independent reflections	5729 [R(int) = 0.0275]
Wavelength	1.54178	Completeness to $\theta$	98.7% ( $\theta = 69.45$ )
Space group	C 2/m	Absorption correction	Numerical
Unit cell dimensions	a= 25.273(5) Å b = 15.103(5) Å c = 19.695(4) Å $\beta$ = 95.233(2) °	Max. and min. transmission	0.82092 and 1.00000
Volume	7486(3) Å <sup>3</sup>	Refinement method	Full-matrix least-squares on F <sup>2</sup>
Z	4	Data/restraints/p arameters	7195/2838/1198
Density	1.653 g/cm <sup>3</sup>	Goodness-of-fit on F2	1.444
Absorption coefficient	0.647	Final R indices $[I > 2\sigma]$	R1 = 0.1194, wR2 = 0.2844
F(0000)	3802	R indices (all data)	R1 = 0.1395, wR2 = 0.2980
Theta range for data collection	3.4110 to 69.4467 °	Largest diff. peak hole	1.834 and -2.038 $e/Å^3$
Index ranges	$\begin{array}{c} -29 \leq h \leq 30 \\ -15 \leq k \leq 18 \\ -23 \leq l \leq 23 \end{array}$		

**Table S3.** Crystal and structure data of  $V_2$ ScN@ $I_h$ (7)-C<sub>80</sub> at 100 K.

Temperature	T = 100 K	Crystal size	$0.26 \times 0.21 \times 0.11 \text{ mm}^3$
Empirical formula	C128 H56 N5 Ni Sc V2	Reflections collected	6101
Formula weight	1875.33	Independent reflections	5084 [R(int) = 0.0337]
Wavelength	1.54178	Completeness to $\theta$	97.2% ( $\theta = 62.490$ )
Space group	C 2/m	Absorption correction	Numerical
Unit cell dimensions	a = 25.2821(15) Å b = 15.1254(10) Å c = 19.7824(16) Å $\beta$ = 94. 8222(6) °	Min. and max. transmission	0.4551 and 0.6933
Volume	7538.1 (9) Å <sup>3</sup>	Refinement method	Full-matrix least-squares on F <sup>2</sup>
Ζ	4	Data/restraints/par ameters	6101/1598/1010
Density	1.652 g/cm <sup>3</sup>	Goodness-of-fit on F2	1.339
Absorption coefficient	3.593	Final R indices $[I > 2\sigma]$	R1 = 0.1234, wR2 = 0.3252
F(0000)	3828	R indices (all data)	R1 = 0.1369, wR2 = 0.3402
Theta range for data collection	3.971 to 62.490 °	Largest diff. peak hole	$1.258 \text{ and } -1.342 \text{ e/Å}^3$
Index ranges	$\begin{array}{c} -28 \leq h \leq 27 \\ -17 \leq k \leq 9 \\ -12 \leq l \leq 22 \end{array}$		

	Sc <sub>3</sub> N@C <sub>80</sub> <sup>[S8]</sup>	$VSc_2 N@C_{80}$	V_ScN@C_80	$LaSc_{2}N@C_{80}^{[S5]}$	$\operatorname{CeSc}_{2}^{N@C} \operatorname{ReSc}_{80}^{[S6]}$	
	Distances (Å)					
Sc-N	1.9931(14) Sc1	2.036(4) Sc1	2.003(6) Sc1a	1.943(6) Sc1	1.942(2) Sc1	
M-N	2.0323(16) Sc2	2.036(4) Sc1a	1.995(5) V1a	1.921(7) Sc2	1.933(2) Sc2	
M-N	2.0526(14) Sc3	1.858(7) V1	2.027(3) V2	2.196(4) La	2.184(2) Ce	
Angles (deg)						
M-N-M	120.70(7) Sc1-N-Sc2	112.1(3) Sc1-N1-V1	119.46(17) Sc1a-N1-V1a	116.88(19) Sc1-N-Sc2	116.87(12) Sc1-N-Sc2	
M-N-M	119.21(6) Sc2-N-Sc3	112.1(3) Sc1a-N1-V1	120.0(3) Sc1a-N1-V2	121.5(3) Sc1-N-La	121.45(11) Sc1-N-Ce	
M-N-M	118.47(7) Sc1-N-Sc3	134.6(5) Sc1-N1-Sc1a	120.5(3) V1a-N1-V2	121.6(3) Sc2-N-La	121.67(11) Sc2-N-Ce	
∑(M-N-M)	358.38	358.8	359.96	360.0	359.99	

Table S4. Selected interatomic distances and angles.

Table S4. Continued.

	$GdSc_{2}N@C_{80}^{[S4]}$	$TbSc_{2}N@C_{80}^{[S4]}$	$ErSc_{2}^{N@C_{80}^{[S7]}}$	$\operatorname{Gd}_{2}\operatorname{ScN@C}_{80}^{[S4]}$	V <sub>2</sub> ScN@C <sub>80</sub>	
		Dista	nces (Å)			
Sc-N	1.916(9) Sc1	1.949(8) Sc1	1.968(6) Sc1	1.911(3) Sc1	2.003(6) Sc1a	
M-N	1.919(8) Sc1	1.949(8) Sc1A	1.968(6) Sc1a	2.072(3) Gd1	1.995(5) V1a	
M-N	2.149(10) Gd	2.126(11) Tb1	2.089(9) Er	2.102(3) Gd2	2.027(3) V2	
Angles (deg)						
M-N-M	117.31(15) Sc1-N1-Gd1	129.0(4) Sc1-N-Tb1	119.1(3) Sc1-N-Er	117.31(15) Sc1-N1-Gd1	119.46(17) Sc1a-N1-V1a	
M-N-M	123.81(16) Sc1-N1-Gd2	116.0(4) Sc1A-N-Tb1	119.1(3) Sc1a-N-Er	123.81(16) Sc1-N1-Gd2	120.0(3) Sc1a-N1-V2	
M-N-M	118.82(14) Gd1-N1-Gd2	115.0(7) Sc1-N-Sc1A	121.3(6) Sc1-N-Sc1a	118.82(14) Gd1-N1-Gd2	120.5(3) V1a-N1-V2	
∑(M-N-M)	359.94	360.0	359.6	359.94	359.96	

S7. UV-vis-NIR spectroscopic analysis of  $V_x Sc_{3-x} N@I_h(7)-C_{80} (x=1, 2)$ .



**Figure S7.** UV-vis-NIR spectra of V<sub>2</sub>ScN@ $I_h(7)$ -C<sub>80</sub> and VSc<sub>2</sub>N@ $I_h(7)$ -C<sub>80</sub> dissolved in CS<sub>2</sub> in comparison with that of Sc<sub>3</sub>N@ $I_h(7)$ -C<sub>80</sub>. Insets: enlarged spectra showing the absorption onsets marked by the arrows.

**Table S5**. Electronic absorption data of  $V_x Sc_{3-x} N@I_h(7)-C_{80}$  (x=1, 2) in comparison with those of  $Sc_3 N@I_h(7)-C_{80}$  and  $TiSc_2 N@I_h(7)-C_{80}$ .

Sample	UV-vis-NIR	Absorption	$\Delta E_{gap, optical}$	Ref.
	absorption peaks	onset ( $\lambda_{onset}$ ,	$/ eV^{[a]}$	
	(nm)	nm)		
$Sc_3N@I_h(7)-C_{80}$	377, 424, 622,	820	1.51	S9
	735			
$VSc_2N@I_h(7)-C_{80}$	313, 385, 748	1700	0.73	this work
$V_2 Sc N@I_h(7)-C_{80}$	327, 603	1290	0.96	this work
$\mathrm{TiSc}_{2}\mathrm{N}@I_{h}(7)-\mathrm{C}_{80}$	330, 605	870	1.43	S10

<sup>[a]</sup>  $\Delta E_{gap, optical}$  (optical band-gap) = 1240 /  $\lambda_{onset}$ .

The UV-vis-NIR spectra of  $V_xSc_{3-x}N@I_h(7)-C_{80}$  (x=1, 2) are compared with those of  $Sc_3N@I_h(7)-C_{80}$  and  $TiSc_2N@I_h(7)-C_{80}$  in Figs. 3 and S7,<sup>[S9,S10]</sup> and their characteristic electronic absorption data are compared in Table S5. For  $VSc_2N@I_h(7)-C_{80}$ , three discernible broad shoulder peaks at about 313, 385 and 748 nm are observed, and the latter two absorption shoulder peaks seem to red-shift compared with the corresponding shoulder peaks observed for  $Sc_3N@I_h(7)-C_{80}$  (377 and 735 nm).<sup>[S11]</sup> Contrarily, the absorption shoulder peaks at 377 and 622 nm observed for  $Sc_3N@I_h(7)-C_{80}$  seem to experience blue-shifts instead in the absorption spectrum of  $V_2ScN@I_h(7)-C_{80}$  in which the shoulder peaks are observed at about 327 and 603 nm. Interestingly, such a blue-shifting change of the absorption peaks of  $Sc_3N@I_h(7)-C_{80}$  is quite similar to that observed for  $TiSc_2N@I_h(7)-C_{80}$ , and the absorption shoulder peaks of  $V_2ScN@I_h(7)-C_{80}$  (330 and 605 nm).<sup>[S10]</sup>

S8. ESR spectra of  $V_x Sc_{3-x} N@I_h(7)-C_{80}$  (x=1, 2).



**Figure S8.** ESR spectra of  $VSc_2N@I_h(7)-C_{80}$  (A) and  $V_2ScN@I_h(7)-C_{80}$  (B) in toluene measured at 130 K.

S9. DFT calculated spin densities of  $V_x Sc_{3-x} N@I_h(7)-C_{80}$  (x=1, 2).



**Figure S9.** DFT calculated spin densities of  $VSc_2N@I_h(7)-C_{80}$  (a) and  $V_2ScN@I_h(7)-C_{80}$  (b) at GGA-PBE/DNP level. V, Sc, N atoms are drawn in orange, red and green, while the isovalues of the blue and yellow isosurfaces are 0.03 and  $-0.03 e/Å^3$ , respectively.

Based on the DMol<sup>3</sup> calculations, we found that the spin states of VSc<sub>2</sub>N@ $I_h(7)$ -C<sub>80</sub> and  $V_2$ ScN@ $I_h(7)$ -C<sub>80</sub> are triplet and quintet, respectively. Besides, we performed additional calculations for both molecules with singlet spin states, and found that they are less stable than triplet/quintet states (the energy difference between the singlet and triplet states for VSc<sub>2</sub>N@ $I_h(7)$ -C<sub>80</sub> is about 300 meV, while that between the singlet and quintet states is about 150 meV for  $V_2ScN@C_{80}$ ). The triplet and quintet spin states of VSc<sub>2</sub>N@ $I_h(7)$ -C<sub>80</sub> and V<sub>2</sub>ScN@ $I_h(7)$ -C<sub>80</sub> are confirmed by calculating their molecular magnetic moments, which are predicted to be 2.0 and 4.0  $\mu_B$  (Bohr magneton), respectively. The atomic magnetic moments of V, N, Sc1, and Sc2 atoms in VSc<sub>2</sub>N@ $I_h(7)$ -C<sub>80</sub> are about 2.15, -0.10, 0.06, 0.09  $\mu_B$ , while those of V1, V2, N, and Sc atoms are respectively about 2.29, 2.28, 0.23, and 0.08  $\mu_B$  in  $V_2$ ScN@ $I_h(7)$ -C<sub>80</sub>. It is evident that the magnetism is mainly contributed by V atom(s) in both VSc<sub>2</sub>N@ $I_h(7)$ -C<sub>80</sub> and V<sub>2</sub>ScN@ $I_h(7)$ -C<sub>80</sub> molecules. This conclusion is further verified by calculating their spin densities, which are defined by the density of the alpha spin (spin-up) and beta spin (spin-down) electrons as shown in Fig. S9, indicating that the spin density is mainly localized on the  $V^{3+}$  ion(s) for both VSc<sub>2</sub>N and V<sub>2</sub>ScN clusters.

Fig. S9 shows the spin densities of  $VSc_2N@I_h(7)-C_{80}$  and  $V_2ScN@I_h(7)-C_{80}$ , in

which the isovalues of the blue and yellow isosurfaces are 0.03 and  $-0.03 \text{ e/Å}^3$ , respectively. Here, the positive (negative) value, illustrating with the blue (yellow) surface, denotes that the density of the spin-up electrons is larger (smaller) than that of the spin-down electrons. Since the spin contamination cannot be explored by reporting  $\langle S^2 \rangle$  values using DMol<sup>3</sup> package, we then performed Gaussian09 calculations, indicating that the  $\langle S^2 \rangle$  values of VSc<sub>2</sub>N@*I*<sub>h</sub>(7)-C<sub>80</sub> and V<sub>2</sub>ScN@*I*<sub>h</sub>(7)-C<sub>80</sub> are predicted to be about 2.09 and 6.24, respectively. These values are close to *s*(*s*+*1*), where *s* =  $1/2 \times [$ number of unpaired electrons], suggesting that the spin contamination with states of higher multiplicities is very slight in both VSc<sub>2</sub>N@*I*<sub>h</sub>(7)-C<sub>80</sub> and V<sub>2</sub>ScN@*I*<sub>h</sub>(7)-C<sub>80</sub>.

S10. Cyclic voltammograms of  $V_x Sc_{3-x} N@I_h(7)-C_{80}$  (x=1, 2) in different scanning regions.



**Figure S10.** Cyclic voltammograms of  $VSc_2N@I_h(7)-C_{80}$  (a) and  $V_2ScN@I_h(7)-C_{80}$  (b) in *o*-DCB solution in different scanning regions showing the correlation of each reduction/oxidation step with the corresponding re-oxidation/re-reduction step. Scan rate: 100 mV•s<sup>-1</sup>, TBAPF<sub>6</sub> as supporting electrolyte. The asterisks label the oxidation peak of ferrocene. Labels of letters A-J are same to those described in Fig. 4.

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