Supporting Information

Scandium carbide/cyanide alloyed cluster inside fullerene cage: synthesis and structural studies of $Sc_3(\mu_3\text{-}C_2)(\mu_3\text{-}CN)@I_h\text{-}C_{80}$

Taishan Wang,[a*] Jingyi Wu,[b] Yongqiang Feng,[a] Chunru Wang[a]

[a] *Key Laboratory of Molecular Nanostructure and Nanotechnology, Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, China. Fax: 86-10-62652120; Tel: 86-10-62652120;*
[b] *Laboratory of Nuclear Analysis Techniques, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing, 100049, China*

E-mail: wangtais@iccas.ac.cn

Experimental Section:

1. Synthesis and purification of $Sc_3(C_2)(CN)@I_h$-C_{80}

Graphite rods were core-drilled and subsequently packed with a mixture of Sc/Ni_2 alloy and graphite powder in a weight ratio of 2:1. These rods were then vaporized in a Krätschmer-Huffman generator under mixed atmosphere of 6 Torr N_2 and 194 Torr He. The resulting soot was Soxhlet-extracted with toluene for 12 h. $Sc_3(C_2)(CN)@I_h$-C_{80} was isolated from various empty fullerenes and other scandium metallofullerenes by multi-stage HPLC.

2. HPLC data of purified $Sc_3(C_2)(CN)@I_h$-C_{80}

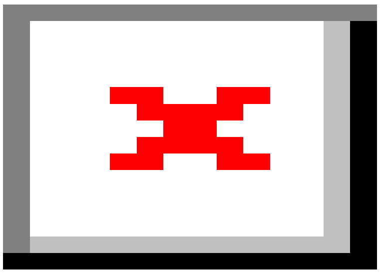


Figure S1. The first stage HPLC profile of toluene extract of the soot containing scandium endohedral metallofullerenes (Φ20×250 mm Buckyprep column; flow rate 12 ml/min; toluene as eluent).

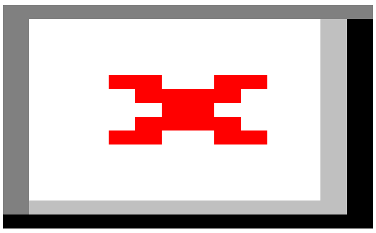


Figure S2. The second stage HPLC profile of isolation of $Sc_3(C_2)(CN)@I_h$-C_{80} (Φ20×250 mm Buckyprep-M column; flow rate 12 ml/min; toluene as eluent).

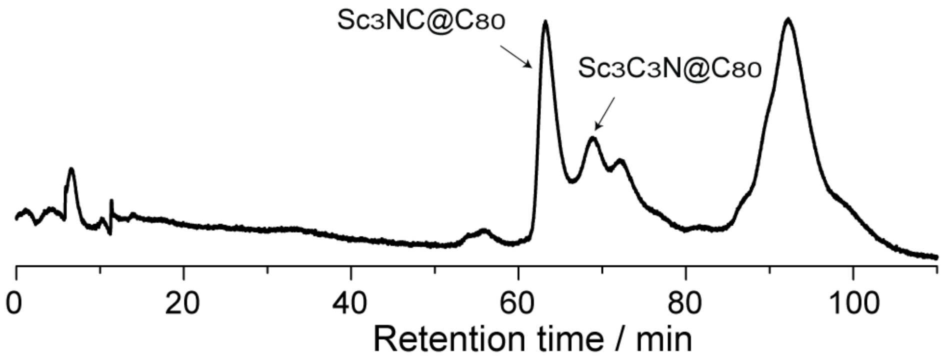


Figure S3. The third stage HPLC profile of isolation of $Sc_3(C_2)(CN)@I_h$-C_{80} (Φ20×250 mm Buckyprep column; flow rate 12 ml/min; toluene as eluent).

3. UV/Vis-NIR spectrum of purified $Sc_3(C_2)(CN)@I_h$-C_{80} compared with those of $Sc_3CN@I_h$-C_{80}, $Sc_3N@I_h$-C_{80}, and $Sc_3C_2@I_h$-C_{80}.

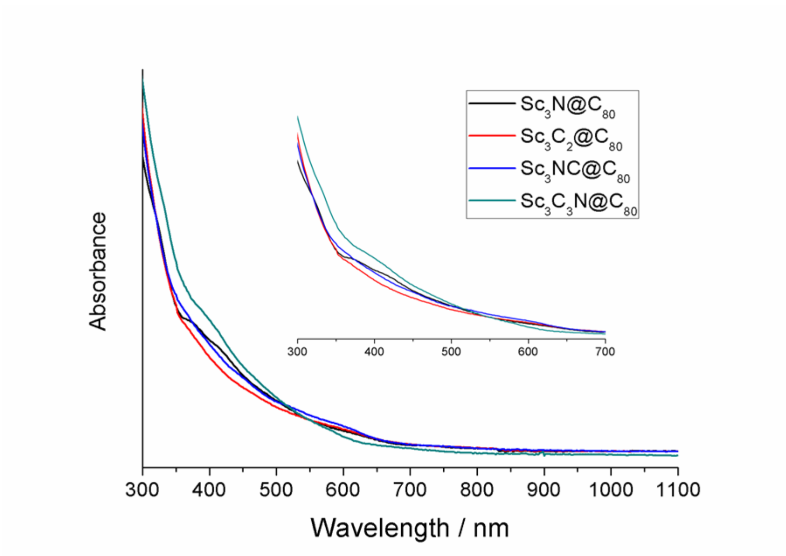


Figure S4. UV/Vis-NIR spectra of purified $Sc_3(C_2)(CN)@I_h$-C_{80}, $Sc_3CN@I_h$-C_{80}, $Sc_3N@I_h$-$C_{80}$and $Sc_3C_2@I_h$-C_{80} in toluene.

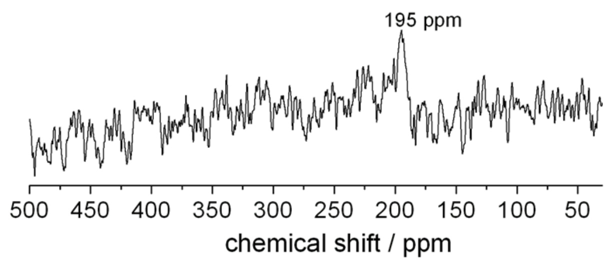


Figure S5. ^{45}Sc NMR (145 MHz) spectrum of $Sc_3(C_2)(CN)@I_h$-C_{80} in CS_2.

3. FTIR and Raman spectra of purified $Sc_3(C_2)(CN)@I_h$-C_{80} compared with those of $Sc_3CN@I_h$-C_{80}, $Sc_3N@I_h$-C_{80}, and $Sc_3C_2@I_h$-C_{80}.

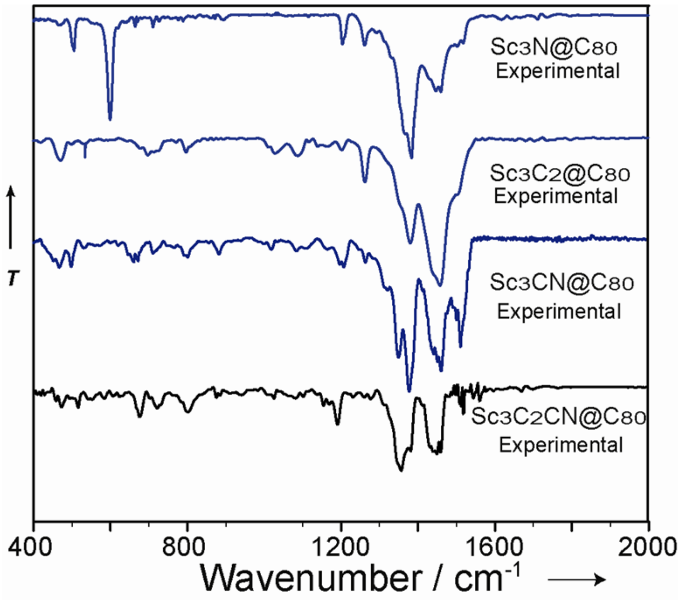


Figure S6. FTIR spectra of $Sc_3(C_2)(CN)@I_h$-C_{80} compared with those of $Sc_3CN@I_h$-C_{80}, $Sc_3N@I_h$-C_{80}, and $Sc_3C_2@I_h$-C_{80}.

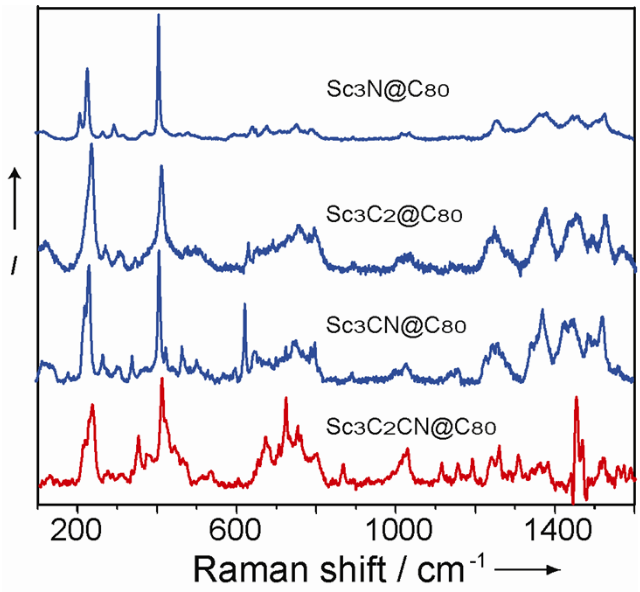


Figure S7. Raman spectra of $Sc_3(C_2)(CN)@I_h$-C_{80} compared with those of $Sc_3CN@I_h$-C_{80}, $Sc_3N@I_h$-C_{80}, and $Sc_3C_2@I_h$-C_{80}. Laser wavelength: 633 nm.

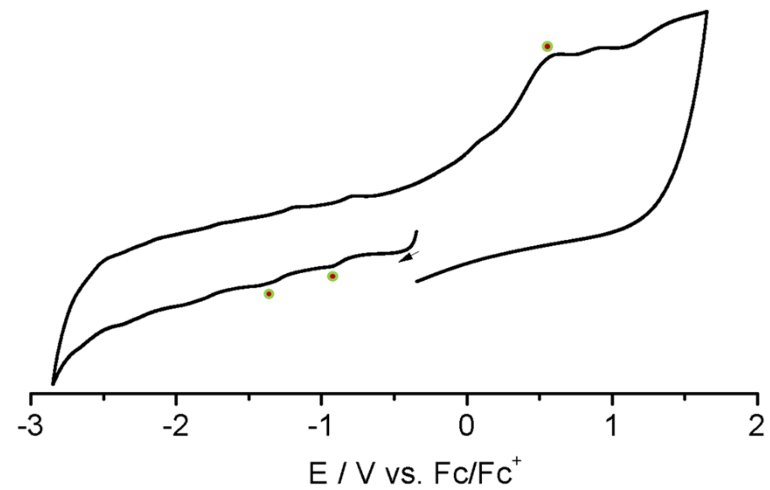


Figure S8. CV spectrum of $Sc_3(C_2)(CN)@I_h\text{-}C_{80}$ in *o*-DCB. 0.05 M $(n\text{-}Bu)_4NPF_6$; scan rate, 100 mV s^{-1}.

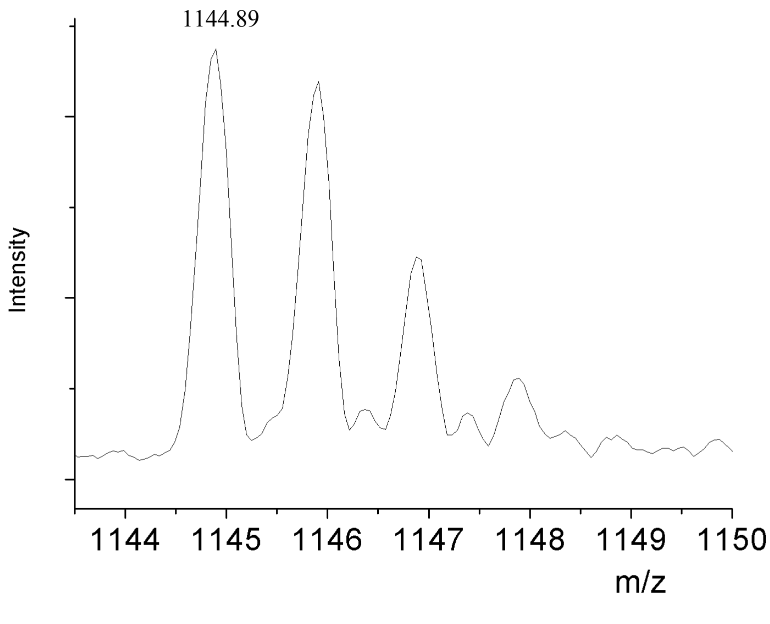


Figure S9. Repeated MALDI-TOF of $Sc_3(C_2)(CN)@I_h\text{-}C_{80}$. The first peak in its isotope distributions locates at 1444.89, the simulated peak is 1444.88.

Computational Section:

5. Geometry of $Sc_3(C_2)(CN)@I_h\text{-}C_{80}$

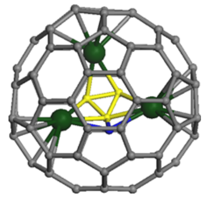
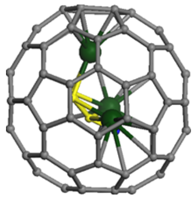
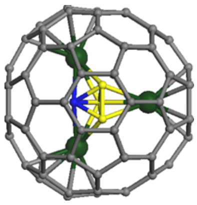
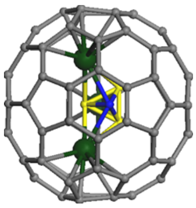
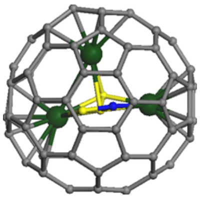
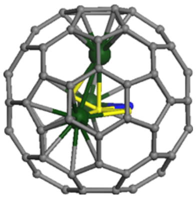
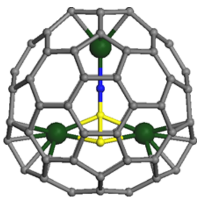
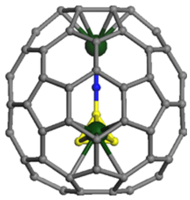
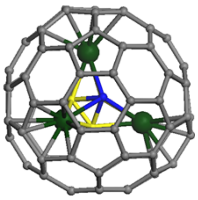
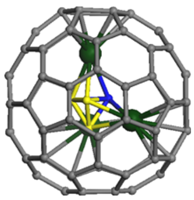
3D representation		Symm.	RE	Eg
Side view	Top view			
		C_1	33.0	0.78
		C_s	47.4	1.20
		C_1	65.9	0.61
		C_{2v}	176.3	0.56
		C_s	44.8	1.36

Fig. S10 Symmetries, 3D ball-stick represent for the GGA-PBE/DNP-optimized various concerned possible isomers of $Sc_3(C_2)(CN)@I_h\text{-}C_{80}$. Relative energies (RE, in kcal/mol) are relative to the ground-state structure, HOMO-LUMO gaps (Eg, eV). Green balls represent the Sc atoms, yellow balls the carbon atoms and blue balls the nitride atoms of the inner carbide moiety, the carbon atoms of the I_h-C_{80} cage are represented by gray balls.

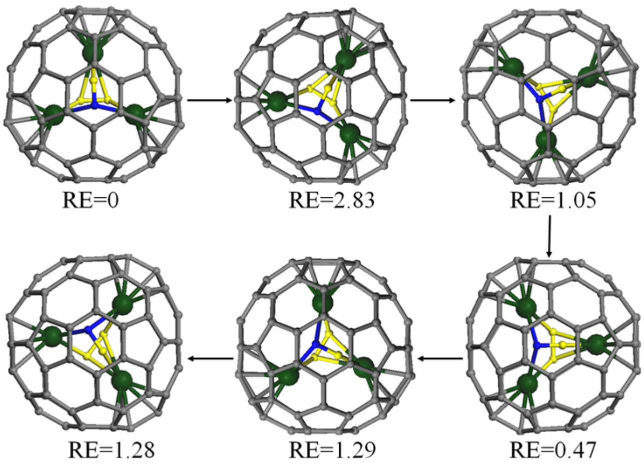


Fig. S11 Selected points along the potential energy surface for the rotation of the $[Sc_3C_3N]^{6+}$ cluster around the C_2-axis of the I_h-C_{80} cage (PBE/DNP calculations). The energies (RE, kcal/mol) are relative to the ground-state structure. Green balls represent the Sc atoms, yellow balls the carbon atoms and blue balls the nitride atoms of the inner carbide moiety, the carbon atoms of the I_h-C_{80} cage are represented by gray balls.

6. Cartesian coordinates of the BLYP/DNP-optimized geometry of $Sc_3(C_2)(CN)@I_h$-C_{80}

C	-1.44560	0.05590	-0.53750
C	-1.17120	0.06450	0.69270
SC	-0.41670	-1.84560	-0.81360
SC	0.52850	-0.06960	2.05490
SC	-0.37540	1.93640	-0.78310
C	-0.01520	-2.65330	-3.10150
C	-1.20830	-3.17520	-2.45830
C	0.00340	-1.40070	-3.81330
C	-1.22280	-0.66830	-3.88380
C	-2.40750	-1.11410	-3.18250
C	-2.39660	-2.32190	-2.41210
C	1.15090	-3.11040	-2.37950
C	-0.77020	-3.96910	-1.29950
C	1.23870	-0.69480	-3.84800
C	-1.21140	0.76130	-3.87580
C	-3.12970	0.05640	-2.73940
C	0.70350	-3.89540	-1.25900
C	-3.17570	-2.33070	-1.20780
C	-2.39080	1.22020	-3.17290
C	2.38510	-2.35330	-2.36020
C	2.40870	-1.15830	-3.13560
C	1.25210	0.74240	-3.84560
C	-1.50650	-3.83330	-0.04610

C	0.02760	1.47240	-3.80430
C	-2.71500	-3.05290	-0.03850
C	-3.90900	-1.17460	-0.75460
C	-3.84070	0.05590	-1.49360
C	1.46670	-3.82870	-0.02100
C	3.14620	-0.00200	-2.69370
C	2.43180	1.17680	-3.13300
C	3.18670	-2.42060	-1.17600
C	-2.36370	2.42070	-2.39130
C	-3.18080	-2.34350	1.13020
C	-0.74620	-3.81250	1.17280
C	-3.90840	-1.18190	0.68740
C	0.02520	2.72180	-3.08610
C	2.72420	-3.14880	-0.01530
C	-3.89410	1.28030	-0.74350
C	0.70280	-3.84250	1.18830
C	-1.16150	3.25660	-2.43340
C	-3.14510	2.43150	-1.18590
C	3.92280	-1.25970	-0.72530
C	3.87270	-0.02490	-1.45860
C	2.42130	2.36720	-2.35090
C	1.19810	3.15050	-2.36020
C	-1.19650	-3.09740	2.33760
C	-2.40120	-2.32790	2.32800
C	-3.85960	0.03980	1.44110
C	-3.89100	1.27090	0.69930
C	3.17100	-2.43230	1.16610
C	1.14760	-3.14420	2.35610
C	-0.71380	4.04320	-1.26980
C	3.90240	-1.26560	0.72300
C	-2.67720	3.13870	-0.01080
C	-0.02590	-2.67060	3.06610
C	3.90280	1.20290	-0.71330
C	0.75990	3.93600	-1.23200
C	3.21240	2.39350	-1.16130
C	2.36440	-2.39760	2.34640
C	-3.14670	2.41710	1.15240
C	-2.43420	-1.14820	3.13310
C	-3.14770	0.02490	2.69460
C	-1.45580	3.90190	-0.01260
C	3.83920	-0.04190	1.45850
C	3.87920	1.18560	0.73060
C	2.74940	3.10410	0.00410
C	-0.02420	-1.48270	3.87190

C	1.51150	3.81780	0.00680
C	-1.25140	-0.72190	3.85350
C	-2.42040	1.18260	3.14790
C	-2.37080	2.37210	2.35380
C	2.37770	-1.20240	3.17120
C	3.16630	2.35510	1.17680
C	-0.69670	3.84160	1.20850
C	3.07580	-0.04060	2.68810
C	1.24820	-0.76660	4.01010
C	-1.24390	0.72530	3.85830
C	0.75080	3.83260	1.21820
C	-1.15580	3.12230	2.37160
C	2.37250	2.33100	2.35630
C	2.37660	1.12680	3.16090
C	1.25010	0.70880	3.99740
C	-0.00360	1.45400	3.86290
C	1.18200	3.11430	2.38150
C	0.00680	2.66210	3.09000
C	1.32220	0.42100	-0.36770
N	1.39010	-0.71180	-0.02940