Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Electron-spin excitation by implanting hydrogen to metallofullerene: the synthesis and spectroscopic characterizations of $Sc_4C_2H@I_h$-C_{80}

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Contents

Experimental Section:

1. The synthesis and purification of $Sc_4C_2H@C_{80}$

The $Sc_4C_2H@C_{80}$-I_h was discovered during the isolation process of $Sc_4C_2@C_{80}$-I_h conformed by MALDI-TOF mass spectrum with a molecular weight 1165. When introducing a certain amount of hydrogen gas in the reaction system, the yield of $Sc_4C_2H@C_{80}$-I_h increased obviously, see Figure S1.

The $Sc_4C_2H@C_{80}$-I_h was synthesized by arc-discharging method. Briefly, the mixture of graphite powder and Sc/Ni_2 alloy with a mass ratio of 1:3 was packed into core-drilled graphite rods. Subsequently the rods were burnt in a Krätschmer-Huffman generator under an atmosphere of 6 Torr H_2 and 194 Torr He. The as-prepared soot was Soxlet-extracted with toluene for 24 h. $Sc_4C_2H@C_{80}$-I_h was isolated and purified by multi-step HPLC. Figure S2 and S3 show HPLC profile of purified $Sc_4C_2H@C_{80}$-I_h sample.

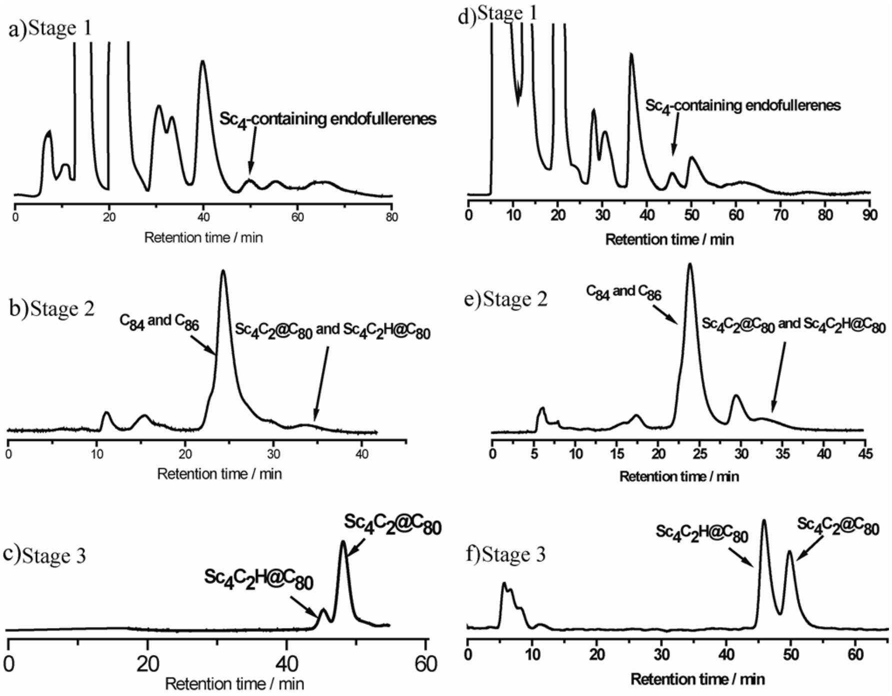

Figure S1. Comparative chromatograms of the isolation process of $Sc_4C_2H@C_{80}$-I_h. (a), (b) and (c) without H_2 in the arc-discharging process, (d), (e) and (f) after introducing H_2. Steps (a), (c), (d) and (f) used a Buckyprep column, and step (b) and (e) were executed on a Buckyprep-M column. (Chromatographic column 20 × 250 mm, toluene as eluent, 12 mL/min). The small amount of $Sc_4C_2H@C_{80}$ observed in Fig. S1b-c was caused by the trace amount of water molecules that provide H element inside the arc-discharging generator. And when we added H_2 into the generator the yield of $Sc_4C_2H@C_{80}$ increased greatly.

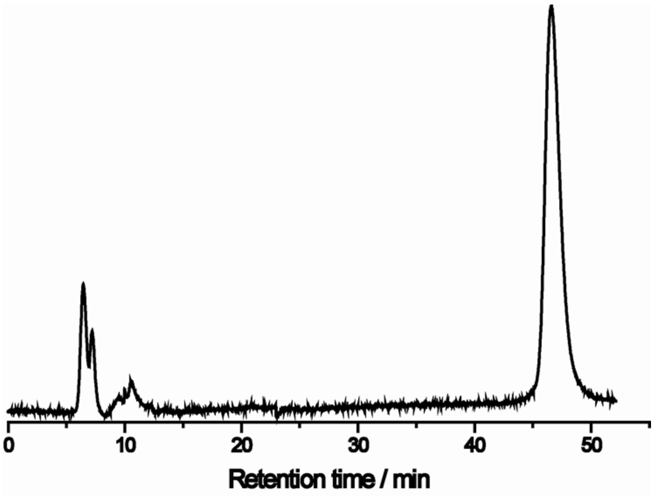

Figure S2. Chromatogram of the isolated $Sc_4C_2H@C_{80}$-I_h (20×250 mm Buckyprep column; flow rate 12 mL/min; toluene as eluent).

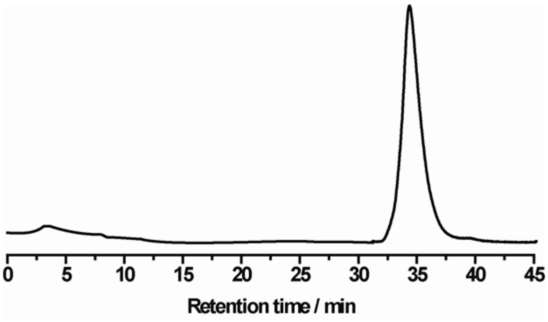

Figure S3. Chromatogram of the isolated $Sc_4C_2H@C_{80}$-I_h (20×250 mm Buckyprep-M column; flow rate 12 mL/min; toluene as eluent).

2. UV-Vis-NIR spectrum of $Sc_4C_2H@C_{80}$

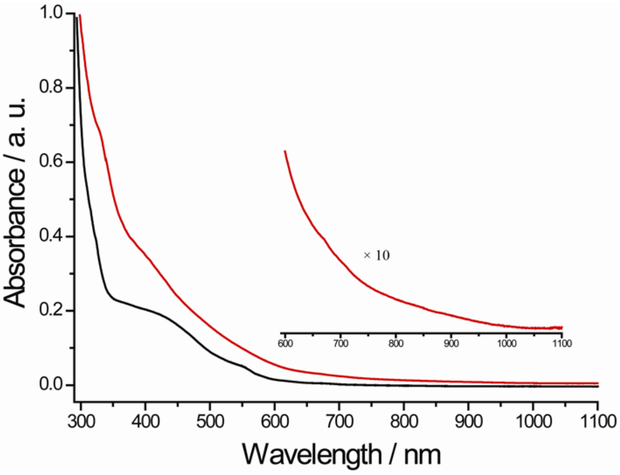

Figure S4. UN-Vis-NIR spectra of $Sc_4C_2H@C_{80}$ (red) and $Sc_4C_2@C_{80}$ (blank). The inset was the enlarged optical absorption region of $Sc_4C_2H@C_{80.}$

3. NMR measurement of $Sc_4C_2H@C_{80}$

NMR experiment was performed on a Bruker NMR spectrometer (600 MHz). The purified $Sc_4C_2H@C_{80}$ sample was dissolved in CS_2 and then sealed in a NMR tube with D_2O inside of a capillary as the internal lock. After 48 h, no any evident NMR signal was observed as shown in Figure S5.

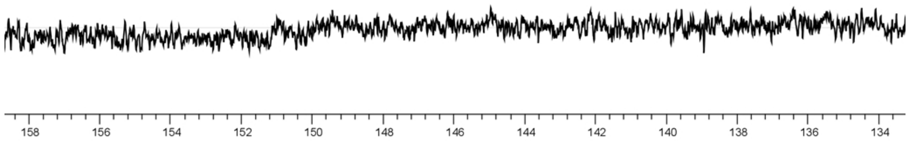

Figure S5. ^{13}C NMR spectrum (CS_2, 150 MHz) of $Sc_4C_2H@C_{80}$. D_2O inside of a capillary was used as an internal lock.

4. CV measurement of $Sc_4C_2H@C_{80}$

Cyclic voltammetry was performed on a CHI660 electrochemical workstation. The experiment was carried out in *o*-DCB solution with 0.05 M $(n\text{-}Bu)_4NPF_6$ using three electrode system, glassy carbon as the working electrode, Pt wire and saturated calomel as the counter and reference electrodes, respectively. All the potentials were referred to the $E_{1/2}$ of Fc/Fc$^+$.

Table S1. Electrochemical potentials (V vs. Fc/Fc$^+$)[a] of $Sc_4C_2H@C_{80}$ and $Sc_4C_2@C_{80}$.

	E_{ox1}	E_{red1}
$Sc_4C_2H@C_{80}$	0.13[a] [0.20][b]	-0.81 [-0.87]
$Sc_4C_2@C_{80}$	-0.05 [0.01]	[-1.53]

[a] the values of half-wave potentials for reversible redox processes.

[b] the peak potentials[ ].

Calculation Section:

All the density functional theory (DFT) computations were performed by using the Dmol3 code[1] with the generalized gradient approximation (GGA) functional of Perdew, Burke, and Ernzerhof (PBE).[2] The IR and Raman spectra were simulated at the B3LYP level with the *Gaussian 03* program.[3,4] The standard 6-31G(d) basis set[5] for C and the small-core RECP (relativistic effective core potential) plus valence double-ζ basis set (LanL2DZ)[6] for Sc were employed, and such a combination of basis sets is denoted as DZP. The geometry of $Sc_4C_2H@C_{80}$ used in the Raman simulation was re-optimized at the B3LYP/DZP level.

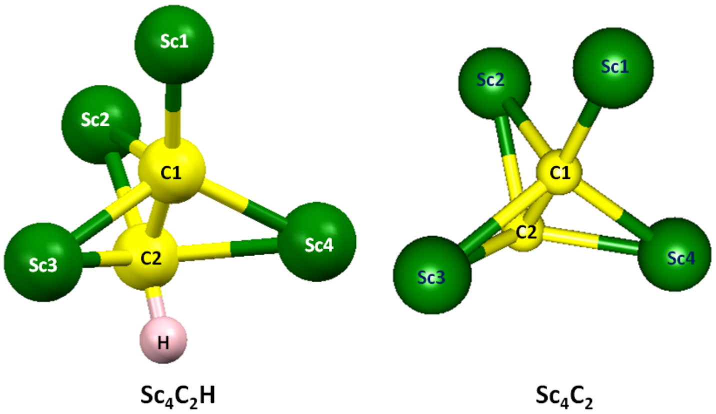

Figure S6. Optimized internal cluster structures of $Sc_4C_2H@C_{80}$ and $Sc_4C_2@C_{80}$

Table S2. Bonding parameters (Å) of internal cluster of $Sc_4C_2H@C_{80}$ and $Sc_4C_2@C_{80}$. (atom labels are shown as Figure S6)

	$Sc_4C_2H@C_{80}$	$Sc_4C_2@C_{80}$
Sc1-Sc2	3.477	3.262
Sc1-Sc3	3.207	3.544
Sc1-Sc4	3.579	3.423
Sc2-Sc3	3.377	3.312
Sc2-Sc4	3.353	3.413
Sc3-Sc4	3.747	3.482
Sc1-C1	1.973	1.965
Sc2-C1	2.266	2.141

Sc3-C1	2.140	2.131
Sc4-C1	2.141	2.130
Sc2-C2	2.045	2.069
Sc3-C2	2.173	2.069
Sc4-C4	2.171	2.067
C1-C2	1.479	1.478
Sc3-H	2.365	
Sc4-H	2.287	
C2-H	1.086	

References

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