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Russian-Doll-Type Metal Carbide Endofullerene: Synthesis, Isolation, and Characterization of $\text{Sc}_4\text{C}_2@C_{80}$ Tai-Shan Wang,^{†,‡} Ning Chen,[†] Jun-Feng Xiang,[†] Bao Li,[†] Jing-Yi Wu,[†] Wei Xu,[†] Li Jiang,[†] Kai Tan,[§] Chun-Ying Shu,^{*,†} Xin Lu,^{*,§} and Chun-Ru Wang^{*,†}

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Endohedral metallofullerenes have broadened the range of fullerenes by virtue of their novel structures and promising applications.^{1,2} To date, the compositions of the endohedral clusters vary, including one metal atom, two metal atoms, and trimetallic nitride, metal carbide, and metal oxide clusters, etc.^{1–6} Because endofullerenes have so many abundant endohedral clusters, they can be provided with intricate structures and properties, such as the quantum gyroscope $\text{Sc}_2\text{C}_2@C_{84}$ as well as $\text{Sc}_4(\mu\text{-O}_2)@C_{80}$ with a distorted tetrahedral scandium oxide cluster inside a carbon cage.^{6,7} For a long time, inorganic nesting polyhedra and carbon anions have attracted much attention because of their distinctive endohedral architectures.⁸ However, metallofullerenes with nesting structures have not been available.^{1,2} Recently, the structure of $\text{Sc}_4\text{C}_2@C_{80-I_h}$ was predicted by density functional theory (DFT) calculations, which revealed that $\text{C}_2@C_{80-I_h}$ is the more realistic formula for Sc_4C_2 .⁹ Herein, we report the synthesis, isolation, and characterization of Sc_4C_2 by means of mass spectrometry (MS) and UV–vis, FTIR, and ^{13}C NMR spectroscopy measurements in combination with DFT calculations and show that the synthesized Sc_4C_2 is indeed $\text{Sc}_4\text{C}_2@C_{80-I_h}$ or, more exactly, $\text{C}_2@C_{80-I_h}$, i.e., a C_2 unit surrounded by a Sc_4 tetrahedron then engaged in an icosahedral C_{80} (C_{80-I_h}) cage.

Sc_4C_2 was prepared by the Krätschmer–Huffman arc discharge method and isolated by two-stage high performance liquid chromatography (HPLC) [see the Supporting Information (SI)]. The soot was promptly Soxhlet-extracted with toluene. HPLC using two columns, namely, Buckyprep and Buckyprep-M, was employed to isolate and purify the Sc_4C_2 , respectively. The purity of the sample was confirmed by HPLC analysis and the MALDI–TOF mass spectrum (Figure 1). The MALDI–TOF mass spectrum exhibits a strong molecular ion peak at m/z 1164, accounting for the production of Sc_4C_2 .

Figure 2 presents the ^{13}C NMR spectrum of Sc_4C_2 in CS_2 at 293 K. Two signals at 137.8 and 144.7 ppm in a 1:3 intensity ratio can be clearly observed. It is unreasonable to identify the molecular structure as $\text{Sc}_4@C_{82}$, as no C_{82} cage can satisfy this ^{13}C NMR spectral pattern. Instead, the spectrum is fully consistent with the C_{80-I_h} cage, which has two unique carbon atoms (the triphenylenic and corannulenic sites) in a 1:3 atomic ratio. Although the Sc_4C_2 endocluster may disturb the chemical environment of the carbon atoms of the C_{80} cage, the influence can be markedly reduced via intramolecular dynamics and cage rotations.^{9,11} To our knowledge, two distinct ^{13}C NMR signals of the C_{80-I_h} cage were also observed for $\text{Sc}_3\text{N}@C_{80-I_h}$ (137.24 and 144.57 ppm),^{3a} $\text{Lu}_3\text{N}@C_{80-I_h}$ (137.4

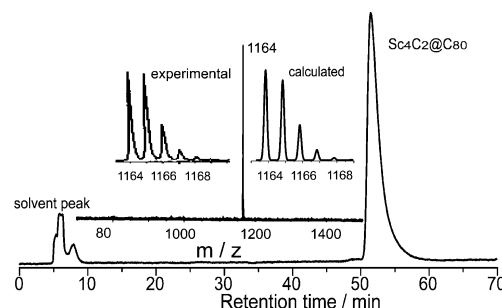


Figure 1. HPLC trace of $\text{Sc}_4\text{C}_2@C_{80-I_h}$ in a Buckyprep column. The inset shows the positive-ion MALDI–TOF mass spectrum as well as the experimental and calculated isotope distributions of $\text{Sc}_4\text{C}_2@C_{80-I_h}$.

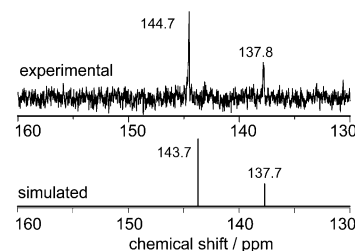


Figure 2. (top) Experimental (CS_2 , 150 MHz) and (bottom) simulated ^{13}C NMR spectra of the C_{80-I_h} cage in $\text{Sc}_4\text{C}_2@C_{80-I_h}$. D_2O inside of a capillary was used as an internal lock.

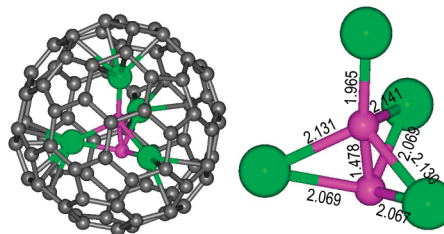


Figure 3. (left) DFT-optimized structure of $\text{Sc}_4\text{C}_2@C_{80-I_h}$ and (right) calculated Sc–C and C–C bond lengths (Å) in the engaged Sc_4C_2 moiety. Green balls represent the Sc atoms and purple balls the carbon atoms of the inner carbide moiety.

and 144.0 ppm),¹⁰ $\text{CeSc}_2\text{N}@C_{80-I_h}$ (135.90 and 142.85 ppm),¹¹ and $\text{Sc}_3\text{C}_2@C_{80-I_h}$ (138.9 and 145.6 ppm).^{5a} As shown in Figure 2, the DFT-predicted ^{13}C NMR spectrum (with signals at 137.7 and 143.7 ppm) for the $\text{Sc}_4\text{C}_2@C_{80-I_h}$ structural model⁹ (Figure 3) agrees well with the experimental ^{13}C NMR spectrum. The ^{13}C NMR chemical shifts of C_2 units within the endocluster, which were calculated to

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Table 1. Experimental and DFT-Calculated Redox Potentials (V) of $\text{Sc}_4\text{C}_2@C_{80}\text{-}I_h$

	αE_2	αE_1	$\text{red}E_1$	$\text{red}E_2$
exptl ^a	1.10	0.40	−1.16	−1.65
DFT ^b	1.30	0.32	−1.33	−2.02

^a Values are given vs Fc/Fc^+ and were obtained in *o*-dichlorobenzene containing 0.1 M TBAPF₆ at a glassy carbon working electrode via CV at a scan rate of 100 mV s^{−1}. ^b From ref 9.

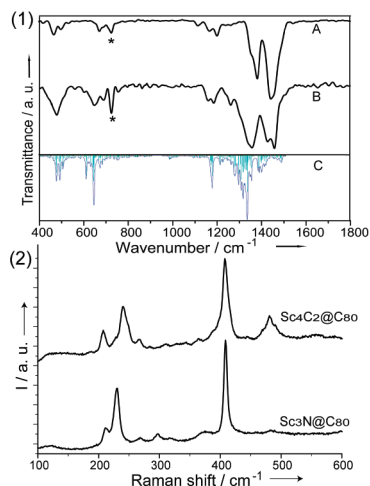


Figure 4. (1) FTIR spectra of (A) $\text{Sc}_3\text{C}_2@C_{80}\text{-}I_h$ and (B) $\text{Sc}_4\text{C}_2@C_{80}\text{-}I_h$ along with (C) the simulated IR spectrum of $\text{Sc}_4\text{C}_2@C_{80}\text{-}I_h$. The asterisks show the solvent peaks. (2) Low-energy Raman spectra of $\text{Sc}_4\text{C}_2@C_{80}\text{-}I_h$ and $\text{Sc}_3\text{N}@C_{80}\text{-}I_h$ (laser wavelength 633 nm).

appear at 226.1 and 326.7 ppm, were not detected because of the spin–rotation interaction and low signal-to-noise ratio.^{5c,9}

Previous DFT computations have shown that $\text{Sc}_4\text{C}_2@C_{80}\text{-}I_h$ has a valence state of $[\text{C}_2]^{6-} @ [\text{Sc}^{3+}]_4 @ [\text{C}_{80}\text{-}I_h]^{6-}$ with a wide HOMO–LUMO gap.⁹ Table 1 lists the redox potentials of $\text{Sc}_4\text{C}_2@C_{80}\text{-}I_h$ obtained by cyclic voltammetry (CV) and DFT computations. The measured electrochemical band gap of 1.56 eV, along with the DFT prediction (1.65 eV), indicates that $\text{Sc}_4\text{C}_2@C_{80}\text{-}I_h$ is a very stable metallofullerene.

The FTIR spectra of $\text{Sc}_4\text{C}_2@C_{80}\text{-}I_h$ and $\text{Sc}_3\text{C}_2@C_{80}\text{-}I_h$ and the DFT-simulated IR spectrum of $\text{Sc}_4\text{C}_2@C_{80}$ are shown in Figure 4. First of all, the experimental FTIR spectrum of $\text{Sc}_4\text{C}_2@C_{80}$ agrees well with the previously DFT-computed IR spectrum⁹ of $\text{Sc}_4\text{C}_2@C_{80}\text{-}I_h$ (Figure 4). The peaks ranging from 1600 to 1000 cm^{−1} can be considered as a group of tangential cage modes of the outer carbon cage.¹² The characteristic vibrations of the tangential cage modes are approximately at 1184, 1359, 1459, and 1513 cm^{−1} for $\text{Sc}_4\text{C}_2@C_{80}\text{-}I_h$. These tangential cage modes of $\text{Sc}_4\text{C}_2@C_{80}\text{-}I_h$ exhibit quite a degree of resemblance to those of the well-known species $\text{M}_3\text{N}@C_{80}\text{-}I_h$ (M = Sc, Dy, Tm, Gd).¹² The vibrational frequency at 480 cm^{−1} can be assigned to the radial cage mode.¹² Signals at 600, 645, and 688 cm^{−1} represent asymmetric Sc–C_{carbide} stretching vibrations, indicating that there are three kinds of Sc–C_{carbide} stretching modes in $\text{Sc}_4\text{C}_2@C_{80}\text{-}I_h$. This assignment is in line with the calculated structure, which presents three groups of Sc–C_{carbide} bonds according to the various bond lengths (Figure 3).

The low-energy Raman spectrum of $\text{Sc}_4\text{C}_2@C_{80}\text{-}I_h$ (Figure 4) shows a resemblance to those of $\text{Sc}_3\text{N}@C_{80}\text{-}I_h$, $\text{Dy}_3\text{N}@C_{80}\text{-}I_h$, and $\text{Sc}_3\text{CH}@C_{80}\text{-}I_h$.¹³ The line groups at ~481 and 240 cm^{−1} are characteristic of the A_g(1)- and H_g(1)-derived cage modes of $\text{C}_{80}\text{-}I_h$, respectively.¹³ It should be noted that the cage modes show obvious splittings, such as those of the A_g(1)-derived modes at 470, 481, and 490 cm^{−1} and the H_g(1)-derived cage modes at 230, 240,

and 249 cm^{−1}. Such big splittings suggest that distortions in the icosahedral C_{80} cage result from presence of the big Sc_4C_2 cluster.^{13c} Two groups of lines at ~208 and 407 cm^{−1} also give splittings caused by the complex structure of the Sc_4C_2 cluster (Figure 3). The medium line at 208 cm^{−1} and weak line at 187 cm^{−1} can be assigned to the Sc_4C_2 translation modes, and the group of lines around 407 cm^{−1} represents the $\nu_s(\text{Sc}\text{--C})$ modes of the Sc_4C_2 moiety.¹³ Therefore, the Raman spectral analysis confirms the $\text{Sc}_4\text{C}_2@C_{80}\text{-}I_h$ structure.

In conclusion, for the first time we have produced stable $\text{Sc}_4\text{C}_2@C_{80}\text{-}I_h$ and characterized it as a metal carbide endofullerene by FTIR and Raman spectra in combination with DFT calculations. Furthermore, DFT calculations have demonstrated that this molecule has a Russian-doll-type structure, $\text{C}_2@C_{80}\text{-}I_h$. To the best of our knowledge, $\text{Sc}_4\text{C}_2@C_{80}\text{-}I_h$ is the first metallofullerene that exhibits a Russian-doll nesting structure.

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Supporting Information Available: Experimental details, UV–vis–NIR spectrum, and CV and HPLC data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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