

Structural and electronic studies of metal carbide clusterfullerene $\text{Sc}_2\text{C}_2@C_5-C_{72}^\dagger$

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We present a metal carbide clusterfullerene $\text{Sc}_2\text{C}_2@C_5(10528)-C_{72}$, whose structure has been baffling for many years. A motional endohedral Sc_2C_2 cluster, special molecule geometry and electronic structure were found in $\text{Sc}_2\text{C}_2@C_5(10528)-C_{72}$. The paramagnetic $\text{Sc}_2\text{C}_2@C_5-C_{72}$ anion radical was successfully prepared by a chemical reduction method and hyperfine couplings in the ESR spectrum were observed.

Endohedral metallofullerenes (EMFs) have attracted increasing interest due to their distinctive nesting structures and unique chemical and physical properties.^{1–7} Especially, metal carbide clusterfullerenes have become a large family with various kinds of cages, endohedral clusters, structures, and properties.^{8–16} The discovery of $\text{Sc}_2\text{C}_2@C_{84}$ proclaimed the emergence of metal carbide clusterfullerenes.¹⁰ Thereafter, many previously reported metal clusterfullerenes, such as $\text{Sc}_2@C_{84}$ and $\text{Sc}_3@C_{82}$, were re-determined to be metallic carbide clusterfullerenes, *i.e.*, $\text{Sc}_2\text{C}_2@C_{82}$ ^{11–13} and $\text{Sc}_3\text{C}_2@C_{80}$,¹⁴ respectively. Of particular note is the recent discovery of $\text{Sc}_2\text{C}_2@C_{2v}-C_{68}$, which is the first metallic carbide clusterfullerene that has a non-IPR fullerene cage.¹⁵ Generally, for these non-IPR metallofullerenes, such as $\text{La}_2@D_2(10611)-C_{72}$,¹⁷ $\text{Sc}_3\text{N}@D_3(6140)-C_{68}$,¹⁸ $\text{Gd}_3\text{N}@C_s(39663)-C_{82}$,¹⁹ $\text{Y}_3\text{N}@C_s(51365)-C_{84}$,²⁰ $\text{Sc}_2\text{S}@C_s(10528)-C_{72}$ ²¹ *etc.*, the internal metal ions bond tightly to the cage motif of a fused-pentagon-pair (FPP) to stabilize the otherwise extremely

unstable non-IPR fullerenes. In these EMFs, XRD studies revealed that the motion of the internal species was nearly inhibited, and ¹³C NMR studies revealed that the chemical shifts of FPP carbon atoms correspondingly appeared at very low field due to the deshielding effect of those tightly attached metal atoms.²² Herein, we report the structural characterizations of another non-IPR carbide clusterfullerene $\text{Sc}_2\text{C}_2@C_5(10528)-C_{72}$. However, this species has been detected by means of mass spectroscopy in previous literature and was mistakenly assumed to be $\text{Sc}_2@C_{74}$.²³ Due to the lack of further characterization, its absolute structure remained uncertain for many years. In our work, this species is unambiguously determined as $\text{Sc}_2\text{C}_2@C_5(10528)-C_{72}$ by a combined study of single-crystal X-ray diffraction (XRD) and ¹³C NMR. In addition, its electronic structure was investigated in detail.

$\text{Sc}_2\text{C}_2@C_{72}$ was prepared using an arc-discharging method and isolated using multi-stage high performance liquid chromatography (HPLC). The purified sample exhibits a single molecular ion peak at *m/z* 978 in the mass spectrum, confirming the chemical composition of $\text{Sc}_2\text{C}_2@C_{72}$. The structure of $\text{Sc}_2\text{C}_2@C_{72}$ was unambiguously characterized by means of the single crystal X-ray diffraction (XRD) method. Black co-crystals of $\text{Sc}_2\text{C}_2@C_{72}$ and nickel(II) octaethylporphyrin ($\text{Ni}^{\text{II}}(\text{OEP})$) were obtained by diffusing a benzene solution of $\text{Sc}_2\text{C}_2@C_{72}$ into a CHCl_3 solution of $\text{Ni}^{\text{II}}(\text{OEP})$. The X-ray structure of $\text{Sc}_2\text{C}_2@C_{72}$ is depicted in Fig. 1 together with an adjacent $\text{Ni}^{\text{II}}(\text{OEP})$ molecule.²⁴ A non-IPR $C_5(10528)-C_{72}$ cage containing a carbide cluster of Sc_2C_2 is clearly identified. This C_{72} cage is different from most previously reported C_{72} species such as $\text{La}_2@D_2(10611)-C_{72}$ ($M = \text{La}, \text{Ce}$),^{17,25} $\text{La}@C_2(10612)-C_{72}$,²⁶ and $C_{72}-C_{2v}(11188)\text{Cl}_4$.^{27,28} Interestingly, surrounding the C_2 carbide unit, the Sc atoms totally have twelve Sc sites including those generated *via* a crystallographic mirror plane; see Fig. S9 in the ESI.† A close inspection reveals that two of the Sc sites (*i.e.*, Sc1 and Sc4A) with fractional occupancies of 0.249 and 0.143, respectively, reside near the pentalenes. However, other Sc sites that represent totally 60.8% metal content reside far from the pentalenes, suggesting a great possibility that the Sc atoms can randomly jump to other sites.

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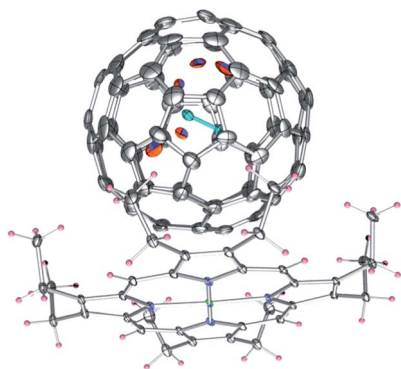


Fig. 1 Ortep drawing of $\text{Sc}_2\text{C}_2@C_s(10528)\text{-C}_{72}\cdot\text{Ni}^{\text{II}}(\text{OEP})$ with 10% thermal ellipsoids, showing intermolecular interactions. The major C_2 carbide unit and the Sc sites having fractional occupancies higher than 0.10 are depicted. The solvent molecules are omitted for clarity. Red: Sc atoms; cyan: carbon atoms in a Sc_2C_2 cluster; black: C_{72} cage atoms.

Such great disordered Sc sites were commonly found in some metallofullerenes having motional endohedral clusters, for example, $\text{Sc}_2\text{C}_2@C_{84}$.^{10,13} This motional behavior of a carbide cluster within a non-IPR cage is entirely unexpected, because in previously studied non-IPR EMFs the endohedral metal atoms always point to the pentalenes and exhibit very restricted motion due to the significant interaction between the metal cations and the pentalenes.^{17–22}

$\text{Sc}_2\text{C}_2@C_{72}$ was further characterized by ^{13}C NMR to study its cage characteristics. As shown in Fig. 2a, the ^{13}C NMR spectrum of $\text{Sc}_2\text{C}_2@C_{72}$ displays 39 signals (33 with full intensity and six with half), which can be unambiguously assigned to the $C_s(10528)\text{-C}_{72}$ cage, and agrees well with the XRD result. Fig. 2c shows the theoretically optimized structure of $\text{Sc}_2\text{C}_2@C_s(10528)\text{-C}_{72}$, in which the encaged Sc_2C_2 cluster has a folding-rhombus-like structure. In particular, the calculation results suggest that the two signals of 161.25 and 161.69 ppm at low field respectively correspond to the two corannulene [6,6,5] carbons (denoted as C34 and C35 in Fig. 2c), whereas the pentalene carbon signals were observed at 133.18–152.14 ppm. These results are very different from most previously reported pentalene carbons, which show NMR signals at lower field relative to other carbons, such as 158.1 ppm for the pentalene carbons in $\text{La}_2@D_2(10611)\text{-C}_{72}$ (ref. 29) and 160.24 ppm for the pentalene motif in $\text{Y}_3\text{N}@C_s(51365)\text{-C}_{84}$.²⁰ This unusual ^{13}C NMR spectrum suggests that the molecule geometry and electronic distribution of $\text{Sc}_2\text{C}_2@C_s(10528)\text{-C}_{72}$ are different from those of other non-IPR metallofullerenes.

Furthermore, ^{45}Sc NMR spectroscopy was employed and a ^{45}Sc NMR signal at 130 ppm was found for $\text{Sc}_2\text{C}_2@C_s\text{-C}_{72}$, indicating its much more shielded Sc atoms relative to those of $\text{Sc}_2\text{S}@C_s\text{-C}_{72}$, which exhibits a ^{45}Sc signal at 183.3 ppm.²¹ It appears that the endohedral C_2 unit imposes a more significant shielding effect on the Sc nuclei than the S unit. Therefore, it is rational to conclude that the endohedral non-metallic units (*i.e.* C_2 and S) can significantly affect their adjacent metal nuclei intramolecular electronic distribution of clusterfullerenes.

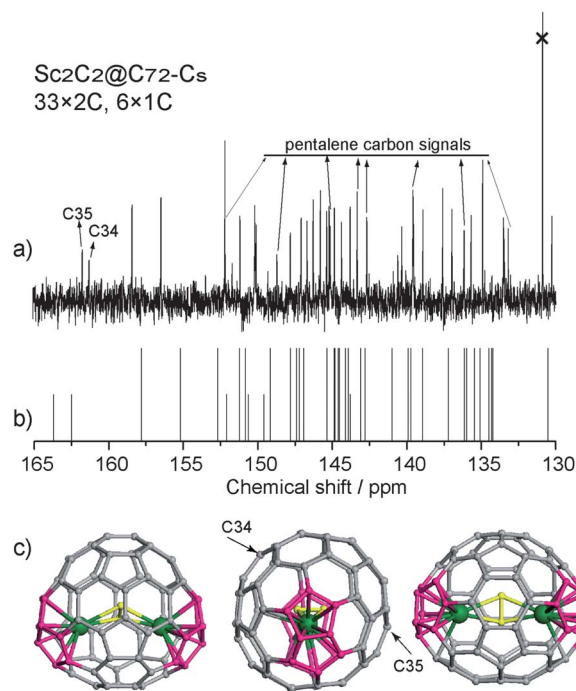


Fig. 2 (a) ^{13}C NMR spectrum (CS_2 , 150 MHz) of $\text{Sc}_2\text{C}_2@C_{72}\text{-C}_s$ showing a $33 \times 2\text{C}$, $6 \times 1\text{C}$ pattern. D_2O inside a capillary was used as an internal lock. The line marked with \times comes from the residual solvent in the sample. (b) Calculated ^{13}C NMR spectrum and (c) optimized structure of $\text{Sc}_2\text{C}_2@C_s(10528)\text{-C}_{72}$ (in different views). Green: Sc atoms; yellow: carbon atoms in a Sc_2C_2 cluster; purple: carbon atoms of two FPPs; gray: C_{72} cage atoms.

As revealed by theoretical calculations, $\text{Sc}_2\text{C}_2@C_s(10528)\text{-C}_{72}$ adopts a closed-shell structure. Analyses of Kohn–Sham wave functions suggested an electronic configuration of $[\text{Sc}^{3+}]_2[\text{C}_2]^{2-}@[\text{C}_{72}]^{4-}$. The redox properties of $\text{Sc}_2\text{C}_2@C_s(10528)\text{-C}_{72}$ were investigated by means of cyclic voltammetry (CV); see Fig. S7 in the ESI.† The first oxidation was observed at 0.41 V while the four reduction peaks appeared at -1.19 , -1.54 , -1.75 , and -2.23 V, respectively. For comparison, the first oxidation of $\text{Sc}_2\text{S}@C_s\text{-C}_{72}$ was observed at 0.75 V while the three reduction peaks appeared at -1.28 , -1.67 , and -2.36 V, respectively.²¹ Considering their identical fullerene cages and endohedral metal ions as well as their similar cluster-to-cage electron-transfer, the obvious redox differences between these two species can be attributed to endohedral non-metal moieties, *i.e.*, $(\text{C}_2)^{2-}$ and S^{2-} units.

In order to further inspect the electronic structure of $\text{Sc}_2\text{C}_2@C_{72}$, electron spin resonance (ESR) spectroscopy was performed on $\text{Sc}_2\text{C}_2@C_{72}$ anion radicals, which were prepared by mixing a THF solution of $\text{Sc}_2\text{C}_2@C_{72}$ with metal potassium under N_2 atmosphere.³⁰ As shown in Fig. 3a, a highly symmetric 15-line ESR spectrum was observed. The simulated ESR spectrum fits well with the experimental data, which corresponds to a splitting value of 0.77 G and a g factor of 2.0050. This result indicates that the spin of the unpaired electron of a $\text{Sc}_2\text{C}_2@C_{72}$ anion radical is delocalized on the carbon cage, which is consistent with the DFT calculations as shown in Fig. 3b.

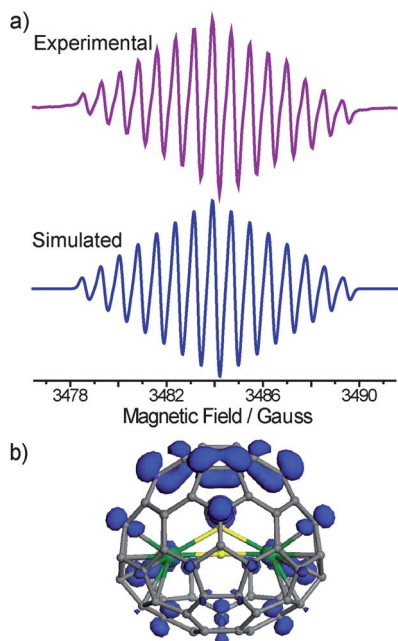


Fig. 3 (a) Measured and simulated ESR spectra of $\text{Sc}_2\text{C}_2@C_s(10528)\text{-C}_{72}$ radical anions. (b) DFT calculated spin density distribution of $\text{Sc}_2\text{C}_2@C_s(10528)\text{-C}_{72}$ radical anions. Green: Sc atoms; yellow: carbon atoms in a Sc_2C_2 cluster; black: C_{72} cage atoms.

Theoretical calculations were performed to document the experimentally obtained hyperfine coupling constants (hfcc) of a $\text{Sc}_2\text{C}_2@C_{72}$ anion radical.^{30–33} The calculated hfcc is -0.71 G for the two equivalent Sc nuclei, which fits well with the experimental result (0.77 G). For comparison, the recently reported ESR spectrum of a metal carbide clusterfullerene $\text{Sc}_2\text{C}_2@C_s(6)\text{-C}_{82}$ anion radical exhibits unsymmetrical characteristics with two different hfcc, $a(\text{Sc}1) = 0.484$ G and $a(\text{Sc}2) = 0.968$ G, and a g factor of 2.00261.³⁴ Different from the two ^{45}Sc hfcc values of a $\text{Sc}_2\text{C}_2@C_{82}$ anion radical, the identical ^{45}Sc hfcc for a $\text{Sc}_2\text{C}_2@C_{72}$ anion radical reflects its higher molecular symmetry as shown in Fig. 2c.

In conclusion, a new endohedral metallofullerene of $\text{Sc}_2\text{C}_2@C_s(10528)\text{-C}_{72}$ that bears two pairs of pentalene motifs has been well characterized. The crystallographic and ^{13}C NMR studies revealed a motional endohedral cluster, special molecule geometry and electronic structure that is different from other non-IPR metallofullerenes. The comparative studies between $\text{Sc}_2\text{C}_2@C_s(10528)\text{-C}_{72}$ and $\text{Sc}_2\text{S}@C_s(10528)\text{-C}_{72}$ disclosed that the endohedral nonmetallic elements (*i.e.* C_2 and S units) can significantly affect the electronic structures of clusterfullerenes as well as the cluster–cage interactions. The paramagnetic $\text{Sc}_2\text{C}_2@C_s\text{-C}_{72}$ anion radical prepared by chemical reduction revealed unique hyperfine couplings between the unpaired electron and two equivalent scandium nuclei. The current discovery demonstrates a crucial complexity in metallofullerene structures that would lead to more profound understanding of fullerene properties and applications.

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