

Mixed Dimetallic Cluster Fullerenes:

ScGdO@C_{3v}(8)-C₈₂ and ScGdC₂@C_{2v}(9)-C₈₂

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ABSTRACT: Mixed-metal cluster fullerenes (MMCFs) have been extensively studied in recent years for their rich structural variability of the encaged clusters and showed great potentials in the applied studies such as biomedicine and molecular electronic devices. However, the study on this field mostly concentrated on the nitride cluster fullerene, very few other type of mixed-metal cluster fullerenes have been reported so far. Herein, we report the synthesis and isolation of the first mixed-metal oxide cluster fullerene, ScGdO@C₈₂, and a novel mixed dimetallic carbide cluster fullerene, ScGdC₂@C₈₂. The spectroscopic and electrochemical studies combined with DFT calculations assigned the molecular structure of the two CFs to ScGdO@C_{3v}(8)-C₈₂ and ScGdC₂@C_{2v}(9)-C₈₂, respectively. DFT calculations also suggest that these two mixed-metal clusters are likely to be found in any of the three IPR C_s(6)-C₈₂, C_{3v}(8)-C₈₂ and/or C_{2v}(9)-C₈₂ cages. The electrochemical studies show that the electrochemical gap of ScGdO@C_{3v}(8)-C₈₂ and

ScGdC₂@C_{2v}(9)-C₈₂ are 1.49 and 1.08 V. Moreover, the comparative studies of ScGdO@C_{3v}(8)-C₈₂ and Sc₂O@C_{3v}(8)-C₈₂, ScGdC₂@C_{2v}(9)-C₈₂ and Sc₂C₂@C_{2v}(9)-C₈₂ showed that, despite their close structural resemblance, the replacement of one Sc ion by Gd ion resulted in notable changes on their electrochemical behaviors as well as their ⁴⁵Sc NMR spectra.

INTRODUCTION

Clusterfullerenes (CFs), formed by encapsulation of clusters inside the hollow sphere of the carbon cages, have attracted great attention in the fullerene research field, because of their fascinating properties and high stabilities.^{1,2} Recent studies suggested that they have great potential in applied studies of biomedicines, molecular electronic devices, catalysis, and solar cells.^{1,3-6} Among them, mixed-metal clusterfullerenes (MMCFs) are of special interests as different metal ions could be incorporated into a single encaged cluster, which brings remarkable structural variability to the MMCFs. So far the most studied MMCFs are the mixed-metal nitride cluster fullerenes (MMNCFs). A series of MMNCFs, such as DySc₂N@C_{2n} (2n = 68, 70, 78),^{7,8} M_xSc_{3-x}N@C₈₀ (x = 1–3, M = Y,⁹ La,¹⁰ Gd,¹¹ Tb,¹¹ Er,¹² Dy^{8,13}), M_xSc_{3-x}N@C₆₈ (x = 1–2; M = Tm, Er, Gd, Ho, La),¹⁴ ScYErN@C₈₀,⁹ CeSc₂N@C₈₀,¹⁵ Gd_xM_{3-x}N@C₈₀ (x = 1, 2, M = Ho, Lu),¹⁶ Lu_xM_{3-x}N@C₈₀ (x = 1, 2, M = Gd, Ho),¹⁶ TiM₂N@C₈₀ (M = Sc,¹⁷ Y¹⁸) and V_xSc_{3-x}N@C₈₀ (x = 1, 2)^{19,20} have been reported. Mixed-metal carbide cluster fullerenes represent another family of intensively studied MMCFs, which include TiSc₂C@C₈₀,²¹ TiSc₂C₂@C₈₀,²¹ TiDy₂C@C₈₀,²² TiDy₂C₂@C₈₀,²² TiLu₂C@C₈₀,²³ ErYC₂@C₈₂.²⁴

With the changeable encaged metal, the structure and chemical activity of MMCFs could be tuned from the homometallic CFs.² Chen and co-workers reported the synthesis of a series of 1,3-dipolar cycloaddition products of Sc_xGd_{3-x}N@C₈₀ (x = 0–3).²⁵ The chemical reactivity of

$\text{Sc}_x\text{Gd}_{3-x}\text{N}@C_{80}$ were found altered by the substitution of Sc with Gd within the encaged clusters. Stevenson and co-workers further reported the structural change in $\text{Sc}_x\text{Gd}_{3-x}\text{N}@C_{80}$ ($x = 1-2$), as shorter Sc–N and longer Gd–N bond lengths were observed compared with those in $\text{Sc}_3\text{N}@C_{80}$ and $\text{Gd}_3\text{N}@C_{80}$, respectively.¹¹ Recently, Popov et al. reported a novel MMCCF- $\text{TiLu}_2\text{C}@C_{80}$, in which the encaged TiLu_2C cluster contains an unprecedented double Ti=C bond.²³ The tunable molecular structures and chemical reactivity make MMCFs promising on the applications such as single-molecule magnets (i.e., $\text{Dy}_x\text{Sc}_{3-x}\text{N}@C_{80}$ ($x = 1, 2$),^{26,27} $\text{TiDy}_2\text{C}_2@C_{80}$,²² $\text{TiDy}_2\text{C}@C_{80}$ ²²) and novel relaxation agents (i.e., $\text{Gd}_x\text{Sc}_{3-x}\text{N}@C_{80}$ ($x = 1, 2$)²⁸). Thus, further exploration of novel MMCFs are of interest from the perspectives of both fundamental and applied studies of endohedral fullerenes.

Dimetallic oxide CF was first reported by Stevenson et al.²⁹ Recently, we reported the synthesis and characterization of a series of dimetallic oxide cluster fullerenes (OCFs) with variable cage structures.³⁰⁻³⁴ Herein, for the first time, we report a mixed-metal oxide cluster fullerene (MMOCF), $\text{ScGdO}@C_{82}$. As a side product, we also obtained a novel MMCCF, $\text{ScGdC}_2@C_{82}$. The two cluster fullerenes were characterized by matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) spectrometry, high-performance liquid chromatography (HPLC), ⁴⁵Sc NMR, UV–vis–NIR absorption, cyclic voltammetry, and DFT calculations. The DFT calculations, combined with spectroscopic and electrochemical studies, assigned the molecular structure of the two CFs to $\text{ScGdO}@C_{3v}(8)-C_{82}$ and $\text{ScGdC}_2@C_{2v}(9)-C_{82}$, respectively. Furthermore, we compared spectroscopic and electrochemical properties of $\text{ScGdO}@C_{82}$ and $\text{ScGdC}_2@C_{82}$ to the previously reported $\text{Sc}_2\text{O}@C_{3v}(8)-C_{82}$ ³¹ and $\text{Sc}_2\text{C}_2@C_{2v}(9)-C_{82}$,^{35,36} respectively.

RESULTS AND DISCUSSION

Preparation and Purification. $\text{ScGdO}@C_{3v}(8)\text{-C}_{82}$ and $\text{ScGdC}_2@C_{2v}(9)\text{-C}_{82}$ were synthesized by a modified Krätschmer-Huffman DC arc-discharge method reactor under a He/CO_2 atmosphere (200 Torr of helium with 20 Torr of CO_2 added). The soot was collected and refluxed in chlorobenzene under an argon atmosphere for 12 h. $\text{ScGdO}@C_{3v}(8)\text{-C}_{82}$ and $\text{ScGdC}_2@C_{2v}(9)\text{-C}_{82}$ were isolated and purified by multistage HPLC separations (Figure S1). In Figure 1, the purity of each sample was confirmed by the single peak on the final-stage HPLC chromatograms and the positive mode matrix-assisted laser desorption/ionization-time of flight mass spectrometry (MALDI-TOF MS) spectrum. Further, the isotopic distribution of the experimental spectra of both samples agree well with the corresponding theoretical simulation for $\text{ScGdO}@C_{3v}(8)\text{-C}_{82}$ and $\text{ScGdC}_2@C_{2v}(9)\text{-C}_{82}$, which confirms their molecular formulas.

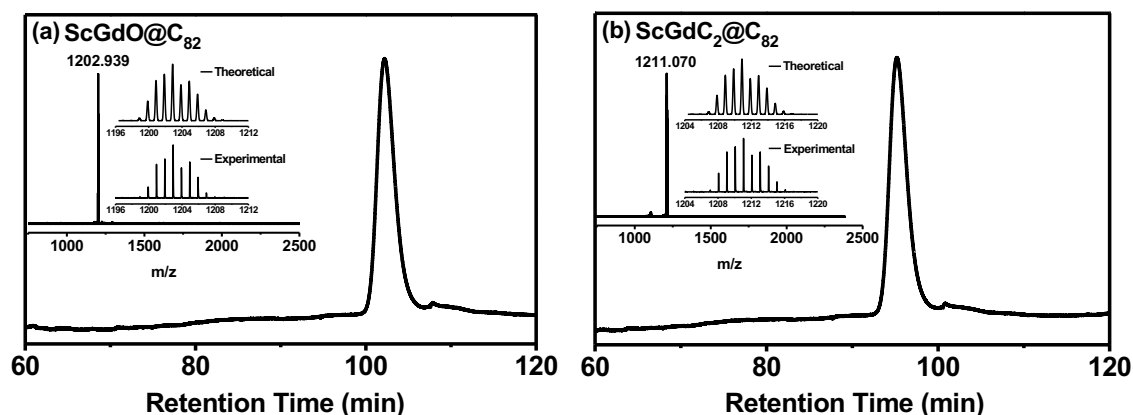


Figure 1. HPLC chromatograms of the $\text{ScGdO}@C_{82}$ (a) and $\text{ScGdC}_2@C_{82}$ (b) obtained on a 10 mm $\times$ 250 mm Buckyprep column with $\lambda = 310$ nm, a flow rate of 4.0 mL/min, and toluene as mobile phase. The insets show mass spectra of the purified $\text{ScGdO}@C_{82}$ and $\text{ScGdC}_2@C_{82}$, and the corresponding experimental and theoretical isotopic distributions.

Spectroscopic Characterization: UV-vis-NIR and ^{45}Sc NMR. The purified samples dissolved in carbon disulfide (CS_2) were characterized by UV-vis-NIR absorption spectroscopy, as shown

in Figure 2. The UV–vis–NIR absorption spectrum of $\text{ScGdO}@C_{82}$ presents two characteristic absorption peaks at 701 and 903 nm, while that of $\text{ScGdC}_2@C_{82}$ shows pronounced peaks at 680, 820 and 910 nm. Previous studies have confirmed that the spectra of endohedral fullerenes are predominantly dependent on π – π^* carbon cage transitions and the cage isomer structure, irrespective of the encapsulated species. The absorption spectrum of $\text{ScGdO}@C_{82}$ showed great resemblance to that of the previously reported $\text{Sc}_2\text{O}@C_{3v}(8)\text{-C}_{82}$,³¹ indicating that they may share the same cage symmetry of $C_{3v}(8)\text{-C}_{82}$ and the electronic structure of $(\text{ScMO})^{4+}@(C_{3v}(8)\text{-C}_{82})^{4-}$ ($M = \text{Sc}$ or Gd). Likewise, the absorption pattern and the characteristic peaks of $\text{ScGdC}_2@C_{82}$, almost identical to those of $\text{Sc}_2\text{C}_2@C_{2v}(9)\text{-C}_{82}$,^{35,36} again suggests that $\text{ScGdC}_2@C_{82}$ may adopt the $C_{2v}(9)\text{-C}_{82}$ cage isomer and has four cluster-to-cage electron transfer. On the other hand, notable differences could be observed between the spectra of $\text{ScGdO}@C_{82}$ and $\text{Sc}_2\text{O}@C_{3v}(8)\text{-C}_{82}$ as well as between $\text{ScGdC}_2@C_{82}$ and $\text{Sc}_2\text{C}_2@C_{2v}(9)\text{-C}_{82}$, which is likely due to the impact of the replacement of Sc by Gd in the respective encapsulated clusters. Similar effects had been reported for the MMNCFs.³⁷ The spectral onsets of $\text{ScGdO}@C_{82}$ and $\text{ScGdC}_2@C_{82}$ are located around 1147 and 1100 nm, respectively, which result in optical band gap of 1.08 and 1.13 eV. Thus, both of the $\text{ScGdO}@C_{3v}(8)\text{-C}_{82}$ and $\text{ScGdC}_2@C_{2v}(9)\text{-C}_{82}$ could be assigned to large optical bandgap fullerenes.

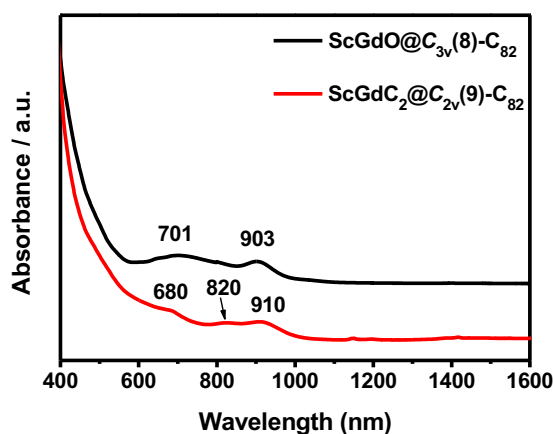


Figure 2. UV-vis-NIR absorption spectra of purified $\text{ScGdO}@C_{3v}(8)\text{-C}_{82}$ and $\text{ScGdC}_2@C_{2v}(9)\text{-C}_{82}$ in CS_2 .

The ^{45}Sc NMR spectra of $\text{ScGdO}@C_{3v}(8)\text{-C}_{82}$ and $\text{ScGdC}_2@C_{2v}(9)\text{-C}_{82}$ are presented in Figure 3. Both of them show broad single line, suggesting that, similar to most of the previously reported cluster fullerenes, both ScGdO and ScGdC_2 cluster rotate inside fullerene cages.^{31,32,34} The chemical shifts recorded at 298 K are 37.6 ($\text{ScGdO}@C_{3v}(8)\text{-C}_{82}$) and 40.8 ($\text{ScGdC}_2@C_{2v}(9)\text{-C}_{82}$) ppm respectively, both of them showing notable shift from their Sc-based single metal clusterfullerenes. Chemical shift of Sc for $\text{ScGdO}@C_{3v}(8)\text{-C}_{82}$ is downshifted from 66.2 ppm for $\text{Sc}_2\text{O}@C_{3v}(8)\text{-C}_{82}$.³¹ Surprisingly, the ^{45}Sc NMR signal for $\text{ScGdC}_2@C_{2v}(9)\text{-C}_{82}$ (40.8 ppm) significantly downshifted from that of the 214 ppm for $\text{Sc}_2\text{C}_2@C_{2v}(9)\text{-C}_{82}$, a rare observation with such a stunning difference.³⁸ With only one encaged metal Sc changed to Gd in these two EMFs, the large chemical shift differences on the ^{45}Sc NMR spectra indicated that chemical shifts of Sc atoms are very sensitive to their neighboring metals incorporated in the encapsulated carbide cluster. On the other hand, interestingly, the ^{45}Sc NMR chemical shifts of $\text{ScGdO}@C_{3v}(8)\text{-C}_{82}$ and $\text{ScGdC}_2@C_{2v}(9)\text{-C}_{82}$ are very close to each other, which might be due to a joint effect from the change of both clusters and the cage isomers.

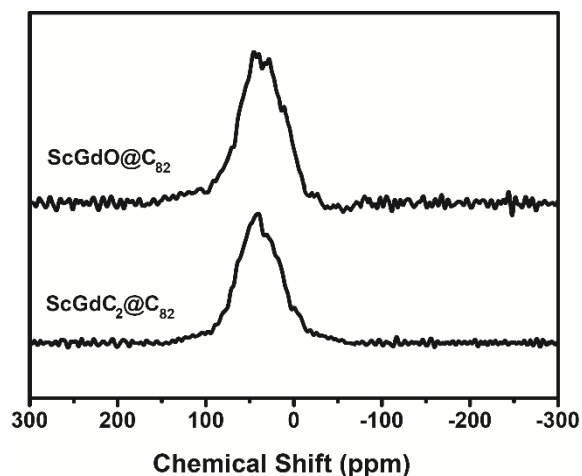


Figure 3. ^{45}Sc NMR spectra of $\text{ScGdO}@C_{3v}(8)\text{-C}_{82}$ and $\text{ScGdC}_2@C_{2v}(9)\text{-C}_{82}$ in CS_2 at room temperature.

Electrochemical Studies. Figure 4 shows the cyclic voltammograms of $\text{ScGdO}@C_{3v}(8)\text{-C}_{82}$ and $\text{ScGdC}_2@C_{2v}(9)\text{-C}_{82}$ measured in *o*-dichlorobenzene (*o*-DCB) solution containing tetrabutylammonium hexafluorophosphate (TBAPF_6) as the supporting electrolyte. The cyclic voltammogram of $\text{ScGdO}@C_{3v}(8)\text{-C}_{82}$ presents a reversible first oxidation step with a half-wave potential at 0.57 V and a second irreversible oxidation step. For the reductive processes, $\text{ScGdO}@C_{3v}(8)\text{-C}_{82}$ exhibits two irreversible reduction steps at -0.92, -1.30 V and one reversible reduction step at -1.72 V, respectively (see Table 1). In general, the redox processes of $\text{ScGdO}@C_{3v}(8)\text{-C}_{82}$ show similar pattern to those of $\text{Sc}_2\text{O}@C_{3v}(8)\text{-C}_{82}$.³¹ The first oxidation process of them are both reversible and the first oxidation potential of them are very close to each other (+0.57 V and +0.54 V, respectively). However, there are notable differences on their reductive processes. The first (-0.92 V) and second (-1.30 V) peak potentials of $\text{ScGdO}@C_{3v}(8)\text{-C}_{82}$ are positively shifted compared to those of $\text{Sc}_2\text{O}@C_{3v}(8)\text{-C}_{82}$ (-1.17 and -1.44 V, respectively), but the third (-1.72 V) peak potential become more negative than that of

$\text{Sc}_2\text{O}@\text{C}_{3v}(8)\text{-C}_{82}$ (-1.55 V), indicating the considerable impact of the substitution of Sc by Gd in the oxide cluster of the corresponding cluster fullerenes. In addition, the electrochemical gap of $\text{ScGdO}@\text{C}_{3v}(8)\text{-C}_{82}$ (1.49 V) also shows difference to that of $\text{Sc}_2\text{O}@\text{C}_{3v}(8)\text{-C}_{82}$ (1.71 V). By contrast, $\text{ScGdC}_2@\text{C}_{2v}(9)\text{-C}_{82}$ exhibit more differences on the electrochemical behavior to $\text{Sc}_2\text{C}_2@\text{C}_{2v}(9)\text{-C}_{82}$ in the oxidative processes, rather than the reductive processes. The first ($+0.34$ V) and second ($+0.76$ V) oxidation potentials of $\text{ScGdC}_2@\text{C}_{2v}(9)\text{-C}_{82}$ are positively shifted compared with those of $\text{Sc}_2\text{C}_2@\text{C}_{2v}(9)\text{-C}_{82}$ ($+0.25$ and $+0.67$ V, respectively),³⁶ while the reduction processes of $\text{ScGdC}_2@\text{C}_{2v}(9)\text{-C}_{82}$ are nearly identical to $\text{Sc}_2\text{C}_2@\text{C}_{2v}(9)\text{-C}_{82}$ (see Table 1). The electrochemical gap of $\text{ScGdC}_2@\text{C}_{2v}(9)\text{-C}_{82}$ (1.08 V) is only slightly larger than that of $\text{Sc}_2\text{C}_2@\text{C}_{2v}(9)\text{-C}_{82}$ (0.99 V). By contrast, the electrochemical gap of $\text{ScGdO}@\text{C}_{3v}(8)\text{-C}_{82}$ (1.49 V) is significantly smaller than that for $\text{Sc}_2\text{O}@\text{C}_{3v}(8)\text{-C}_{82}$ (1.71 V). These results reveal that, for the dimetallic clusters, both the substitution of one metal atom and the change of the non-metal ion could result in a notable influence on their electrochemical behaviors as well as the electronic structures.

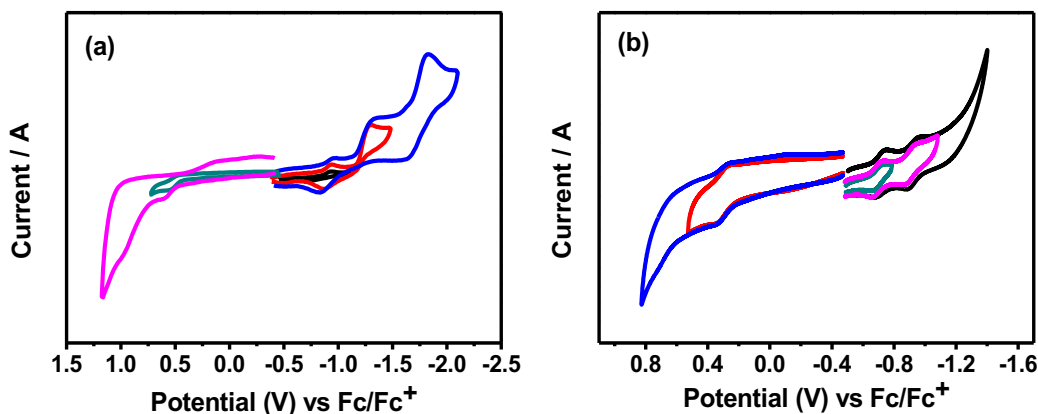


Figure 4. Cyclic voltammograms of ScGdO@C_{3v}(8)-C₈₂ (a) and ScGdC₂@C_{2v}(9)-C₈₂ (b), measured in 0.05 M (*n*-Bu)₄NPF₆/*o*-DCB solution. Ferrocene (Fc) was added as the internal standard, TBAPF₆ as supporting electrolyte, scan rate: 100 mV/s.

Table 1. Redox Potentials (V vs Fc /Fc⁺) of ScGdO@C_{3v}(8)-C₈₂, ScGdC₂@C_{2v}(9)-C₈₂ Obtained in (*n*-Bu)₄NPF₆/*ortho*-Dichlorobenzene with Ferrocene (Fc) as the Internal Standard

Compound	E ^{2+/-}	E ^{+/0}	E ^{0/-}	E ^{-/2-}	E ^{2-/3-}	E ^{3-/4-}	EC _{gap} (V)	ref
ScGdO@C _{3v} (8)-C ₈₂	+0.97 ^b	+0.57 ^a	-0.92 ^b	-1.30 ^b	-1.72 ^a		1.49	this work
Sc ₂ O@C _{3v} (8)-C ₈₂	+1.09 ^b	+0.54 ^a	-1.17 ^b	-1.44 ^b	-1.55 ^b	-1.78 ^b	1.71	31
ScGdC ₂ @C _{2v} (9)-C ₈₂	+0.76 ^b	+0.34 ^a	-0.74 ^a	-0.95 ^a			1.08	this work
Sc ₂ C ₂ @C _{2v} (9)-C ₈₂	+0.67 ^a	+0.25 ^a	-0.74 ^a	-0.96 ^b			0.99	36

^aHalf-wave potential in volts (reversible redox process). ^bPeak potential in volts (irreversible redox process).

Computational Studies on ScGdO@C₈₂. Besides the experimental characterization of ScGdO@C₈₂, we conducted a computational study to find out which isomer is the one obtained in experiments. For the C₈₂ cage, there are 39718 isomers, but only nine of them follow the isolated pentagon rule (IPR).³⁹ The electronic structure of ScGdO@C₈₂ can be described, according to an ionic model of interaction,^{40,41} as (ScGdO)⁴⁺@(C₈₂)⁴⁻. DFT calculations at BP86/TZP level (see Computational Details) predict isomers C_{3v}(8), C_{2v}(9) and C_s(6) as the lowest-energy C₈₂ tetraanions. As a consequence, calculations for these three IPR cages have been carried out on ScGdO@C₈₂. In addition, we have also considered some other cages that do not follow the isolated pentagon rule (non-IPR). In particular, we have chosen the cages with the lowest energies as tetraanions among those that have one or two pairs of adjacent pentagons (APP1 and APP2, respectively). Several orientations of the ScGdO cluster inside the cages were

taken into account, especially for the IPR cages (see Tables S1 and S3 and Figures S2-S9). According to the rather low relative energies shown by many different orientations, one can consider that there is free rotation of the internal mixed-metal cluster inside the three IPR isomers. It seems that internal cluster rotation inside the $C_{3v}(8)$ cage is somewhat favoured compared to the other cages.

Relative energies and free energies up to high temperatures (300 and 2000 K) for the most stable $\text{ScGdO}@C_{82}$ isomers have been analyzed, as shown in Table 2. The most stable orientation for each $\text{ScGdO}@C_{82}$ cage is represented in Figure 5. The lowest-energy C_{82} tetraanion is the $C_{3v}(8)$ cage, and the same isomer is also found to be the most stable after encapsulation of ScGdO . Isomers $\text{ScGdO}@C_s(6)-C_{82}$ and $\text{ScGdO}@C_{2v}(9)-C_{82}$ show rather low relative energies and free energies (Table 2). Encapsulation energy for $\text{ScGdO}@C_{3v}(8)-C_{82}$ (-8.14 eV) is larger than for $\text{ScGdO}@C_s(6)-C_{82}$ and $\text{ScGdO}@C_{2v}(9)-C_{82}$ (-7.43 and -7.42 eV, respectively). We have confirmed that for these isomers there is indeed a formal transfer of four electrons from the cluster to the cage, with formally Sc^{3+} , Gd^{3+} and O^{2-} (see Figure S10). Gd^{3+} ions show seven unpaired f electrons which confer them a local magnetic moment of $S=7/2$ (see spin density plot in Figure S11). The optimized Sc-O-Gd angles for $\text{ScGdO}@C_s(6)-C_{82}$ and $\text{ScGdO}@C_{3v}(8)-C_{82}$ are 148 and 146°, respectively, which are somewhat smaller than those found in the already characterized $\text{Sc}_2\text{O}@C_s(6)-C_{82}$ (162°) and $\text{Sc}_2\text{O}@C_{3v}(8)-C_{82}$ (156°). The Sc-O and Gd-O distances are rather similar for the three isomers, around 1.86 Å for Sc-O and 2.06 Å for Gd-O. The larger Gd-O distance compared to Sc-O induces a compression of the Gd-O-Sc angle compared to Sc-O-Sc and makes the ScGdO cluster to have a different orientation as that for the Sc_2O cluster inside the $C_{3v}(8)-C_{82}$ cage (see Figure S12). The average M-Cage distances are shorter for $M=\text{Sc}$ than for $M=\text{Gd}$ as expected.⁴²

Table 2. Number of adjacent pentagon pairs (APP), relative energies (ΔE), relative free energies at 300 and 2000 K (ΔG), HOMO-LUMO (H-L) gaps, M-O and average M-Cage (M=Sc, Gd) distances, and Sc-O-Gd angles for the lowest-energy ScGdO@C₈₂ OCFs.^{a)}

ScGdO@C ₈₂	APP	ΔE	ΔG 300 K	ΔG 2000 K	H-L gap	Sc-O	Gd-O	Sc-Cage ^{b)}	Gd-Cage ^{b)}	Sc-O-Gd
C _s (6)	0	1.4	0.7	0.0	0.763	1.869	2.054	2.390	2.642	148.2
C _{3v} (8)	0	0.0	0.0	3.4	0.973	1.859	2.056	2.405	2.703	146.1
C _{2v} (9)	0	2.2	1.5	2.0	0.468	1.861	2.054	2.404	2.727	151.7
C _{2v} (39705)	1	25.5	23.8	20.2	0.302	1.878	2.162	2.476	2.694	178.9
C ₁ (36652)	2	48.0	45.8	41.4	0.232	1.878	2.091	2.443	2.718	157.6

^{a)} Energies in kcal·mol⁻¹, H-L gaps in eV, distances in Å and angles in degrees. H-L gap corresponds to that of alpha orbitals (unrestricted-DFT formalism due to the unpaired f electrons in Gd). ^{b)} Average for those M-Cage distances shorter than 2.53 Å for Sc and 2.88 Å for Gd.

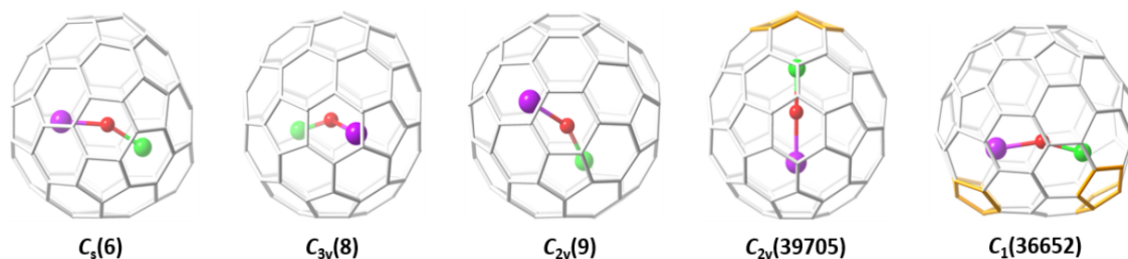


Figure 5. Representations of the lowest-energy DFT-optimized isomers of ScGdO@C₈₂. Color code: oxygen in red, Sc in green and Gd in purple. Pentalene motifs are highlighted in orange.

To have more insight on the relative stabilities and to predict the abundances of the five computed ScGdO@C₈₂ isomers (see Table 2) at the high temperatures of fullerene formation in the arc, their molar fractions up to 5000 K have been computed using the rigid rotor and

harmonic oscillator (RRHO) approximation and the related free-encapsulating model (FEM) as proposed by Slanina and co-workers (Figure 6).^{43,44}

ScGdO@C_{3v}(8)-C₈₂ is predicted to be the most abundant isomer at low temperatures within the FEM model ($T < 600$ K) and the most stable one in the whole range of temperatures within the RRHO approximation. ScGdO@C_s(6)-C₈₂ is predicted to be the second most abundant isomer by RRHO and the most abundant one at temperatures higher than 600 K by the FEM model. ScGdO@C_{2v}(9)-C₈₂ is not found to be predominantly abundant at any temperature range by neither the FEM nor RRHO approximations. The predicted abundances for the APP1 and APP2 isomers are negligible, especially for the latter.

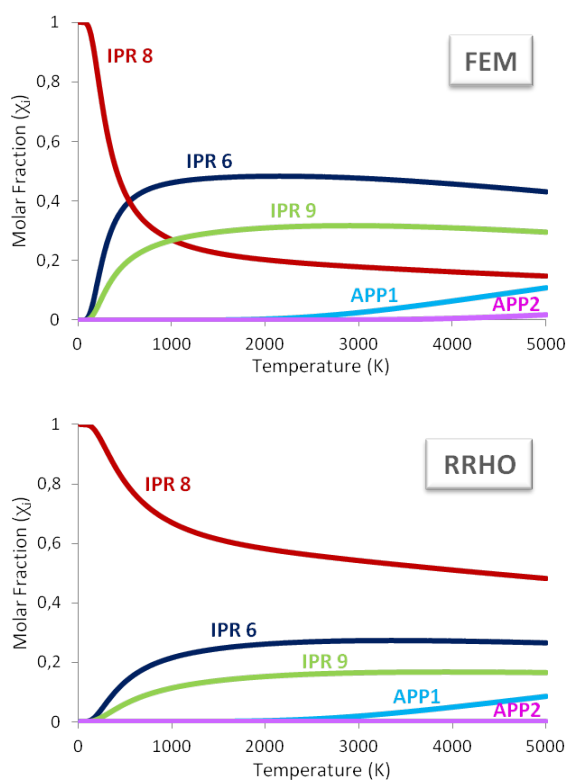


Figure 6. Predicted molar fractions as a functions of the temperature using the free-encapsulating model (FEM) and the rigid rotor and harmonic oscillator (RRHO)

approximation for the lowest-energy isomers of ScGdO@C₈₂. APP1 and APP2 isomers correspond to ScGdO@C_{2v}(39705)-C₈₂ and ScGdO@C₁(36652)-C₈₂, respectively.

We have estimated the oxidation and reduction potentials for the most abundant isomers; ScGdO@C_s(6)-C₈₂, ScGdO@C_{3v}(8)-C₈₂ and ScGdO@C_{2v}(9)-C₈₂ (see Table 3). The isomer that best matches the experiment is ScGdO@C_{3v}(8)-C₈₂. The computed (and experimental) first oxidation and reduction potentials for ScGdO@C_{3v}(8)-C₈₂ are 0.38 V (0.57 V) and -1.18 V (-0.92 V), respectively. Even though the computed potentials are cathodically shifted compared to experiments by 190 (oxidation) and 160 mV (reduction), the computed EC gap (1.56 V) agrees well with the experiment (1.49 V). The predicted first oxidation potentials for the other two isomers are significantly smaller than the experimental value, by 360 mV for C_s(6)-C₈₂ and 480 mV for C_{2v}(9)-C₈₂. These considerable differences in the anodic potentials, much larger than the average error of our methodology,^{45,46} as well as the differences in the EC gap make us discard each of these two isomers to be the one isolated and characterized. We have also computed the UV-vis-NIR spectrum for ScGdO@C_{3v}(8)-C₈₂, which is in rather good agreement with experiment (see Figure S13 and Table S5).

Table 3. Computed oxidation and reduction potentials, electrochemical (EC) gaps and HOMO-LUMO (H-L) gaps for the three most-abundant ScGdO@C₈₂ isomers.^{a)}

ScGdO@C ₈₂	E ^{2+/+}	E ^{+/0}	E ^{0/-}	E ^{-/2-}	EC	H-L gap
C _s (6)	0.72	0.20	-1.04	-1.46	1.24	0.773
C _{3v} (8)	0.88	0.38	-1.18	-1.47	1.56	0.954
C _{2v} (9)	0.58	0.09	-0.82	-1.26	0.91	0.478

Experimental	0.97	0.57	-0.92	-1.30	1.49
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^{a)} Oxidation and reduction potentials and EC gaps in V and H-L gaps in eV. H-L gap corresponds to that of alpha orbitals (unrestricted-DFT formalism due to the unpaired f electrons in Gd).

Therefore, by combining experimental results and computations, we predict isomer ScGdO@C_{3v}(8)-C₈₂ to be the one isolated and characterized. However, the observation of isomers ScGdO@C_s(6)-C₈₂ and/or ScGdO@C_{2v}(9)-C₈₂ could be possible in future experiments.

Computational Studies on ScGdC₂@C₈₂. We did an analogous analysis for the novel mixed dimetallic carbide cluster fullerene ScGdC₂@C₈₂. The electronic structure of ScGdC₂@C₈₂ can be also described as (ScGdC₂)⁴⁺@(C₈₂)⁴⁻, as for the case of the MMOCF. Therefore, the same three IPR isomers C_s(6)-C₈₂, C_{3v}(8)-C₈₂ and C_{2v}(9)-C₈₂ have been selected to be the candidates for our MMCCF. Besides, we have also considered the lowest-energy APP1 and APP2 tetraanionic cages. It is interesting to note here that, so far, metal carbide cluster fullerenes of the type M₂C₂ (M = Sc, Y, Er) have been already detected in these three IPR cages.^{36,47-49} In this work, however, only one C₈₂ isomer that encapsulates ScGdC₂ has been found. Relative energies of several orientations of ScGdC₂ inside the C_s(6)-C₈₂, C_{3v}(8)-C₈₂ and C_{2v}(9)-C₈₂ cages as well as the non-IPR cages are listed in Table S6. The different geometries for each isomer are represented in Figures S14-S20. The three IPR isomers are almost quasi-energetic; the lowest-energy isomer is ScGdC₂@C_{3v}(8)-C₈₂, followed by ScGdC₂@C_{2v}(9)-C₈₂ and ScGdC₂@C_s(6)-C₈₂ at only 0.2 kcal·mol⁻¹, and 0.6 kcal·mol⁻¹, respectively (see Table 4). The APP1 cage ScGdC₂@C_{2v}(39705)-C₈₂ is at 17.5 kcal·mol⁻¹ and the lowest-energy tetraanionic APP2 cage, once encapsulated, ScGdC₂@C_{2v}(36652)-C₈₂, is at 33.6 kcal·mol⁻¹. Interestingly, two other APP2 cages with more appropriate locations of the pentalene motifs lead to MMCCF with significantly lower energies comparable to that of the APP1 cage (see Table 4). The most

favored orientation for each $\text{ScGdC}_2@\text{C}_{82}$ cage is represented in Figure 7. We have also considered the dimetallofullerenes $(\text{ScGd})^{6+}@\text{C}_{84}^{6-}$, which share stoichiometry with $\text{ScGdC}_2@\text{C}_{82}$ species. In particular, we have computed those $\text{ScGd}@\text{C}_{84}$ isomers that come from the lowest-energy hexaanionic cages, namely, IPR cages $D_2(21)\text{-C}_{84}$ and $D_{2d}(23)\text{-C}_{84}$ and APP1 cage $C_s(51365)\text{-C}_{84}$, which is the largest non-IPR cage found in a clusterfullerene (see Table S2). As observed for other M_2C_{2n} families, the dimetallofullerenes show lower relative energies than the carbide CFs.⁵⁰⁻⁵² The non-IPR $\text{ScGd}@\text{C}_s(51365)\text{-C}_{84}$ is around 15 kcal mol⁻¹ lower in energy than the most-favored IPR carbide CFs whereas the IPR $\text{ScGd}@\text{D}_2(21)\text{-C}_{84}$ and $\text{ScGd}@\text{D}_{2d}(23)\text{-C}_{84}$ are 1.5 and 9.5 kcal mol⁻¹ below (see Table 4). Gibbs free energies have been calculated at different temperatures (300 and 2000 K, see Table 4). $\text{ScGdC}_2@\text{C}_{2v}(9)\text{-C}_{82}$ becomes the most stable carbide CF isomer at 300 K with the dimetallofullerenes $\text{ScGd}@\text{D}_2(21)\text{-C}_{84}$ and $\text{ScGd}@\text{C}_s(51365)\text{-C}_{84}$ at 5.6 and 11.4 kcal mol⁻¹ below (see Table 4). Importantly, the IPR carbide CFs become more stable than the $\text{ScGd}@\text{C}_{84}$ isomers at temperatures of fullerenes formation (around 2000 K), as observed for other M_2C_{2n} families.⁵⁰⁻⁵²

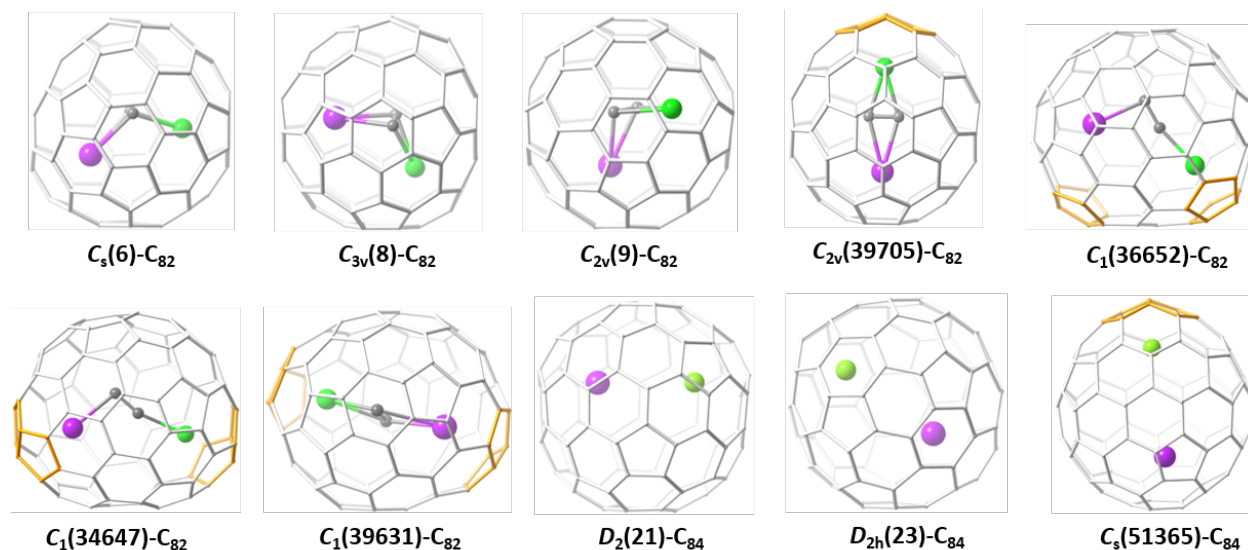


Figure 7. Representations of the lowest-energy DFT-optimized isomers of ScGdC₂@C₈₂ and ScGd@C₈₄. Color code: C₂ in grey, Sc in green and Gd in purple. Pentalene motifs are highlighted in orange.

Table 4. Number of adjacent pentagon pairs (APP), relative energies (ΔE), relative free energies at 300 and 2000 K (ΔG) and HOMO-LUMO (H-L) gaps for the lowest-energy ScGdC₂@C₈₂ and ScGd@C₈₄ CFs.^{a)}

ScGdC ₈₄ isomers	APP	ΔE	ΔG 300 K	ΔG 2000 K	H-L gap
ScGdC ₂ @C _s (6)-C ₈₂	0	0.6	0.4	0.1	0.750
ScGdC ₂ @C _{3v} (8)-C ₈₂	0	0.0	0.5	3.7	0.875
ScGdC ₂ @C _{2v} (9)-C ₈₂	0	0.2	0.0	0.0	0.551
ScGdC ₂ @C _{2v} (39705)-C ₈₂	1	17.5	15.8	11.7	0.220
ScGdC ₂ @C ₁ (36652)-C ₈₂	2	33.6	32.2	28.3	0.456
ScGdC ₂ @C ₁ (34647)-C ₈₂	2	23.6	22.7	19.6	0.685
ScGdC ₂ @C ₁ (39631)-C ₈₂	2	16.7	16.2	14.7	0.614
ScGd@D ₂ (21)-C ₈₄	0	-9.5	-5.6	11.4	0.355
ScGd@D _{2d} (23)-C ₈₄	0	-1.5	1.8	17.1	0.635
ScGd@C _s (51365)-C ₈₄	1	-14.9	-11.4	3.3	0.445

^{a)} Energies in kcal·mol⁻¹, H-L gaps in eV, distances in Å and angles in degrees. H-L gap corresponds to that of alpha orbitals (unrestricted-DFT formalism due to the unpaired f electrons in Gd).

From inspection of the Sc-C and Gd-C distances and Sc-C-Gd angles (see Table S8), the optimized structure of ScGdC₂@C_{2v}(9)-C₈₂ exhibits average Sc-C and Gd-C distances slightly larger than those for isomers ScGdC₂@C_s(6)-C₈₂ and ScGdC₂@C_{3v}(8)-C₈₂. In addition, it also

presents an average Sc-C-Gd angle that is larger than for the other isomers. Therefore, we can infer that the ScGdC₂ cluster fits somewhat better inside the C_{2v}(9)-C₈₂ cage.⁴² The carbide cluster is not planar in any of the IPR cages with Sc-C-C-Gd dihedral angles around 114 degrees (see Table S8). For non-IPR cages, which are somewhat less spherical, i.e. more elongated, the carbide cluster stays almost planar and in some cases the η^2 -coordination of the carbide is even lost (see Figures S14-S20). The M-Cage distances for the four-atom ScGdC₂ cluster are somewhat smaller than for the three-atom ScGdO in line with their different sizes.

We have also computed the molar fractions as function of temperature using FEM and RRHO approximations (see Figure 8). The most abundant isomer at low temperatures and up to 1500 K (1000 K for RRHO) is the APP1 dimetallofullerene ScGd@C_s(51365)-C₈₄. The predominant isomer at T > 1500 K is ScGdC₂@C_{2v}(9)-C₈₂. ScGdC₂@C_s(6)-C₈₂ is predicted to be the second most abundant isomer for T > 1500 K (1000 K for RRHO) and as abundant as ScGdC₂@C_{2v}(9)-C₈₂ at T > 2500K within the FEM model. Isomer ScGdC₂@C_{3v}(8)-C₈₂ is the third most abundant isomer in the range between 2000 and 3000 K. Remarkably, the abundance of isomer APP1 ScGdC₂@C_{2v}(39705)-C₈₂ grows appreciably with temperature to be comparable to ScGdC₂@C_{3v}(8)-C₈₂ at around 3400 K. Hence, it seems rather likely that ScGdC₂@C_{2v}(9)-C₈₂ could be the isomer detected in experiments.

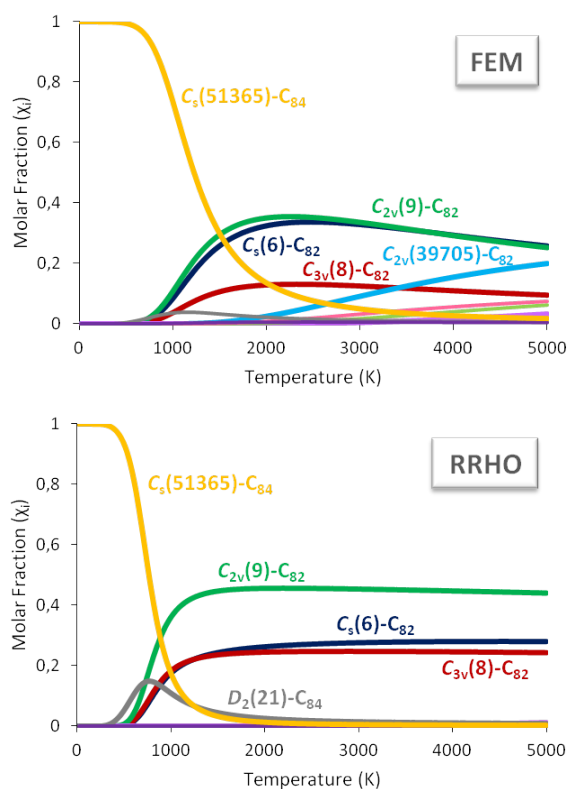


Figure 8. Predicted molar fractions as functions of the temperature using the free-encapsulating model (FEM) and the rigid rotor and harmonic oscillator (RRHO) approximation for the lowest-energy isomers of $\text{ScGdC}_2@\text{C}_{82}$ and $\text{ScGd}@\text{C}_{84}$. See SI for more details.

To help to determine the cage in the isolated $\text{ScGdC}_2@\text{C}_{82}$, we have also computed the oxidation and reduction potentials for the three most abundant isomers (see Table 5). The predicted first oxidation potentials for the three isomers, when compared to experiment, are within the error of our computational methodology (less than 230 mV). The computed first reduction potentials, however, allow us to discard isomers $\text{ScGdC}_2@C_s(6)-C_{82}$ and $\text{ScGdC}_2@C_{3v}(8)-C_{82}$, with differences of 270 and 450 mV, respectively (see Table 5). Besides, the predicted electrochemical gap for $\text{ScGdC}_2@C_{2v}(9)-C_{82}$ (0.92 V), which is the lowest among the three isomers in correlation with the lowest HOMO-LUMO gap, fits the experiment (1.08 V) within

the error of the methodology. In fact, $\text{ScGdC}_2@\text{C}_{2v}(9)\text{-C}_{82}$ is the isomer with the smallest mean absolute error (MAE) when computing the first oxidation/reduction potentials and the EC gap. Finally, the computed UV-vis-NIR spectrum for $\text{ScGdC}_2@\text{C}_{2v}(9)\text{-C}_{82}$ is also in good agreement with experiment (see Figure S22 and Table S9). Therefore, the combination of experiments and computations make us predict, in this case, isomer $\text{ScGdC}_2@\text{C}_{2v}(9)\text{-C}_{82}$ as the one isolated and characterized. Nevertheless, detection and/or isolation of IPR cages $\text{C}_s(6)\text{-C}_{82}$ and $\text{C}_{3v}(8)\text{-C}_{82}$ in the future experiments is also possible, as seen for other clusters.

Table 5. Computed oxidation and reduction potentials, electrochemical (EC) gaps and HOMO-LUMO (H-L) gaps for the three most abundant $\text{ScGdC}_2@\text{C}_{82}$ isomers.^{a)}

$\text{ScGdC}_2@\text{C}_{82}$	$\text{E}^{+/0}$	$\text{E}^{0/-}$	EC	H-L gap
$\text{C}_s(6)$	0.20	-1.01	1.21	0.756
$\text{C}_{3v}(8)$	0.43	-1.19	1.62	0.898
$\text{C}_{2v}(9)$	0.11	-0.81	0.92	0.541
Experimental	0.34	-0.74	1.08	

^{a)} Oxidation and reduction potentials and EC gaps in V and H-L gaps in eV.

CONCLUSIONS

Two novel mixed dimetallic cluster fullerenes $\text{ScGdO}@\text{C}_{3v}(8)\text{-C}_{82}$ and $\text{ScGdC}_2@\text{C}_{2v}(9)\text{-C}_{82}$ have been synthesized, isolated and characterized by mass spectrometry, UV-vis-NIR, cyclic voltammetry, ^{45}Sc NMR and DFT calculations. The spectroscopic and electrochemical studies combined with DFT computations preliminarily assigned the cage symmetry of $\text{ScGdO}@\text{C}_{82}$ and $\text{ScGdC}_2@\text{C}_{82}$ to $\text{C}_{3v}(8)\text{-C}_{82}$ and $\text{C}_{2v}(9)\text{-C}_{82}$, respectively. Therefore, each mixed-metal cluster selects a different cage to be encapsulated, even though the same formal charge transfer of four

electrons is found for the two cluster fullerenes. As a consequence of the small energy differences between the three most stable $C_s(6)-C_{82}$, $C_{3v}(8)-C_{82}$ and $C_{2v}(9)-C_{82}$ tetraanions, the selection of the parent fullerene cage by a given cluster could be altered by little subtleties such as the size of the cluster or the slightly different metal-to-cage interactions. Consequently, though not observed in this work, $ScGdO@C_s(6)-C_{82}$, $ScGdO@C_{2v}(9)-C_{82}$, $ScGdC_2@C_s(6)-C_{82}$ and/or $ScGdC_2@C_{3v}(8)-C_{82}$ could still be obtained in future experiments. Dimetallofullerenes $ScGd@C_{84}$, which show low energies compared to carbide $ScGdC_2@C_{82}$ isomers, are predicted to have low abundances at the high temperatures of fullerene formation, as found for other C_{2n} families. The ^{45}Sc NMR results indicate that the chemical shifts of Sc atoms in the encaged mixed dimetallic cluster $ScGdO$ or $ScGdC_2$ are quite sensitive to the encapsulated clusters. Electrochemical studies reveal that, for the dimetallic clusters, both the substitution of one metal atom and the change of the non-metal ion in the cluster could result in a notable influence on their electrochemical behaviors. Moreover, the incorporation of Gd^{3+} ion inside the fullerene cage provides these clusterfullerenes with a significant magnetic moment ($S=7/2$) in their interior, which make them to be potentially applicable, as for example, to magnetic resonance imaging.

EXPERIMENTAL SECTION

Preparation and Isolation. $ScGdO@C_{3v}(8)-C_{82}$ and $ScGdC_2@C_{2v}(9)-C_{82}$ were synthesized in a modified arc-discharge Krätschmer-Huffman reactor with a mixture of $Sc_2O_3/Gd_2O_3/graphite$ powder (molar ratio of $M/M/C = 1:1:24$), respectively, under a He/CO_2 atmosphere (200 Torr of helium with 20 Torr of CO_2 added). The raw soot was extracted using chlorobenzene as a solvent in a Soxhlet extractor for 12h. The extract was further subjected to a multistage HPLC (Japan Analytical Industry Co., Ltd.) procedure to isolate and purify product with toluene as mobile

phase at the flow rate of 4.0 mL/min. The UV detector was set to 310 nm and a combination of Buckyprep-M column (25 × 250 mm, Cosmosil, Nacalai Tesque Inc.), Buckyprep-D column (10 × 250mm, Cosmosil, Nacalai Tesque, Japan), and Buckyprep (10 × 250mm, Cosmosil, Nacalai Tesque, Japan). The purity of the isolated products were further checked by HPLC using a 10mm × 250 mm Buckyprep column (Nacalai Tesque, Japan) with the flow rate of 4.0 mL/min. The corresponding MALDI-TOF (Ultra-flexxtreme, Bruker, Germany) data for the isolated products are shown in Figure 1.

Spectroscopic and Electrochemical Studies. UV-vis-NIR spectra of the purified products were measured in CS₂ solution with a Cary 5000 UV-vis-NIR spectrophotometer (Agilent, U.S.A). The ⁴⁵Sc NMR spectroscopic measurements were performed at 145 MHz with an Agilent Direct-Drive II 600 MHz spectrometer (Agilent, U.S.A.) at room temperature in CS₂ with D₂O as the lock and a 0.2 M Sc(NO₃)₃ solution in D₂O as the reference. Cyclic voltammetry (CV) was carried out in *o*-dichlorobenzene containing 0.05M (*n*-Bu)₄NPF₆ as supporting electrolyte. A conventional three-electrode cell consisting of a platinum counter electrode, a glassy carbon working electrode, and a silver reference electrode was used for measurement. The CV was measured at scan rate of 100 mV/s.

Computational Details. The geometry optimizations were performed at density functional theory (DFT) level with the ADF 2013 program. The exchange-correlation functionals of Becke and Perdew (BP86) and the Slater TZP basis sets (BP86/TZP level) were used. Relativistic corrections were included by means of the ZORA formalism. Since the gadolinium cation has an incomplete f shell (4f⁷), the spin-unrestricted algorithm is used. The UV-vis-NIR spectrum for ScGdO@C_{3v}(8)-C₈₂ and ScGdC₂@C_{2v}(9)-C₈₂ were computed at BP86/TZP level for C and Gd and at BP86/TZ2P for Sc and O using time-dependent (TD) DFT for wavelengths larger than

450 nm. Oxidation and reduction potentials were calculated at BP86/TZP level with the inclusion of solvent effects by means of the continuous conductor-like screening model (COSMO).^{53,54} To define the cavity that surrounds the molecules we use the solvent-excluding surface (SES) method and a fine tesserae. The radii of the atoms, which define the dimensions of the cavity surrounding the molecule, were chosen to be 2.00 Å for Sc, 1.52 Å for O, 1.08 Å for Gd and 1.70 Å for C.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website. HPLC profiles for the separation of ScGdO@C_{3v}(8)-C₈₂ and ScGdC₂@C_{2v}(9)-C₈₂ and supplementary computational results (relative energies of C₈₂ tetraanions, representation of the computed different orientations of the ScGdO and ScGdC₂ clusters inside the different IPR, APP1 and APP2 cages, fragment interaction diagram for ScGdO@C_{3v}(8)-C₈₂, computed UV-vis-NIR spectra and most intense transitions, xyz coordinates for the lowest-energy structures). A data set collection of computational results is available in the ioChem-BD repository⁵⁵ and can be accessed via <https://doi.org/10.19061/iochem-bd-2-28> (under embargo now). The link for the reviewers to access temporary during the peer review process is

<https://iochem-bd.urv.es/browse/reviewcollection/100/509/51db321eccc5b4160e4625a>.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

The authors declare no competing financial interest.

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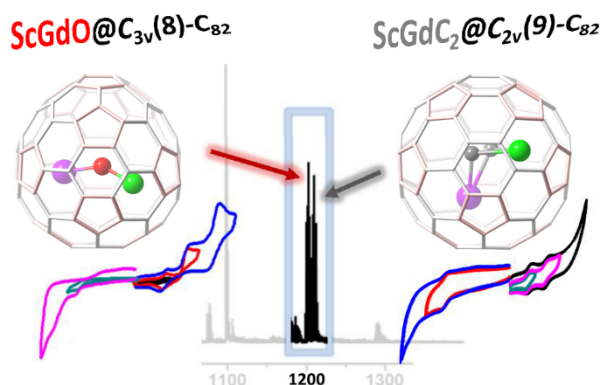
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Synopsis:

The synthesis and isolation of the first mixed-metal oxide cluster fullerene, ScGdO@C₈₂, and a novel mixed dimetallic carbide cluster fullerene, ScGdC₂@C₈₂ were reported. Two compounds

were characterized by mass spectrometry, UV-vis-NIR, cyclic voltammetry, ^{45}Sc NMR spectra and DFT calculations. UV-vis-NIR and DFT calculations assigned the molecular structure of the two CFs to $\text{ScGdO}@C_{3v}(8)\text{-C}_{82}$ and $\text{ScGdC}_2@C_{2v}(9)\text{-C}_{82}$, respectively.