may acclimatize males physiologically and psychologically to the extremely high levels of circulating testosterone[3,4].

This translocation ended the killing of rhinoceros by elephants. Introducing higher-ranking males may help in other reserves containing Kruger orphans where managers face similar problems. In elephant populations that have experienced massive poaching, the hunters' selection of larger males may cause similar problems once rhinoceros populations increase, and these too may be helped by importing older male elephants.

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Materials science

C₆₆ fullerene encaging a scandium dimer

The geometry of carbon cages (fullerenes) is governed by the isolated-pentagon rule (IPR)[1,2], which states that the most stable fullerenes are those in which all pentagons are surrounded by five hexagons. Although this rule has been verified experimentally[3–5], it is impossible for fullerenes in the range C_{60} to C_{70} to obey it. Here we describe the production and characterization of an IPR-violating metallofullerene, $Sc_2@C_{66}$, a C_{66} fullerene encaging a scandium dimer. Our results indicate that encapsulation of the metal dimer significantly stabilizes this otherwise extremely unstable C_{66} fullerene.

We generated soot containing $Sc_2@C_{66}$ and other scandium metallofullerenes[3,4] in direct-current arc discharge of scandium/graphite composite rods under a flow of helium. $Sc_2@C_{66}$ metallofullerene was isolated using multistage high-performance liquid chromatography[6]. Starting with 800 g arc-generated soot, we were able to isolate about 2.0 mg $Sc_2@C_{66}$. The purity (99.8%) of this material was confirmed by laser-desorption time-of-flight mass spectrometry.

There are several ways in which the IPR can be violated, the most straightforward being to generate the so-called 'fused-pentagon' in which pentagons are adjacent to one another. For 66-atom carbon cages with hexagonal and pentagonal faces, there are 4,478 possible (non-IPR) structural isomers with $2 \times D_3$, $1 \times C_{3v}$, $18 \times C_{2v}$, $112 \times C_s$, $211 \times C_2$ and $4,134 \times C_1$ symmetry[7]. Considering the observed 19-lines (5×2; 14×4) in the high-resolution ^{13}C NMR spectrum of $Sc_2@C_{66}$ (Fig. 1a), only eight structural isomers of C_{66} with C_{2v} symmetry can satisfy this ^{13}C NMR pattern.

To determine the geometrical structure of the metallofullerene unambiguously, we made synchrotron X-ray powder diffraction

measurements on $Sc_2@C_{66}$ at SPring-8 BL02B2. The MEM (maximum-entropy method)[5,8] three-dimensional electron-density distribution of $Sc_2@C_{66}$ obtained by the MEM/Rietveld procedure[5,8] using synchrotron X-ray diffraction is shown in Fig. 1b, together with an optimized geometry of $Sc_2@C_{66}$ based on non-local density-function B3LYP/Basis set [Sc(LanL2DZ); C(3-21G)] calculations (Fig. 1c).

The $Sc_2@C_{66}$ X-ray crystal structure is of space group $Pmn2_1$(no. 31), where a is 10.552(2) Å, b is 14.198(2) Å, c is 10.553(1) Å, and the reliability factors of the final Rietveld fitting were $R_{wp} = 2.4\%$ and $R_I = 13.1\%$. The final charge densities obtained by the maximum-entropy method, whose reliability factor is $R_F = 5.4\%$, reveal a pair of two-fold fused pentagons on a C_{66}–C_{2v} cage that encapsulates a Sc_2 dimer; the most stable $Sc_2@C_{66}$ structure has the

least number and degree of fused pentagons out of the 4,478 possible isomers (see Supplementary Information).

The ^{13}C NMR spectrum of $Sc_2@C_{66}$ shows five highly deshielding lines above 151 p.p.m. up to 167.9 p.p.m. These unusual ^{13}C NMR lines stem from those carbon atoms on the fused-pentagon area. In particular, the two lowest lines at half intensity (numbers 16 and 17 in Fig. 1a) originate from the four carbon atoms that connect two pentagonal rings.

The $Sc_2@C_{66}$ structure (Fig. 1c) contains two pairs of two-fold fused pentagons with two closely situated scandium atoms. The observed Sc–Sc distance is 2.87(9) Å, indicative of the formation of a Sc_2 dimer inside the C_{66} cage. Endohedral metallofullerenes are stabilized by intrafullerene electron transfer[3–5,9,10]; there are 40.0(2) e electrons in the area corresponding to the Sc_2 dimer calculated from the MEM charge density, a value that is very close to $(Sc_2)^{2+}$ with 40 e. The *ab initio* calculation also indicates that the Sc_2 dimer donates two electrons to the C_{66} cage, resulting in a formal electronic state of $(Sc_2)^{2+}@C_{66}^{2-}$. It is this charge-transfer interaction between the Sc_2 dimer and the fused pentagons that significantly decreases the strain energies caused by the pair of fused pentagons and thus stabilizes the fullerene cage. We conclude that the isolated-pentagon rule is not necessarily a test for stable geometry in endohedral metallofullerenes[9].

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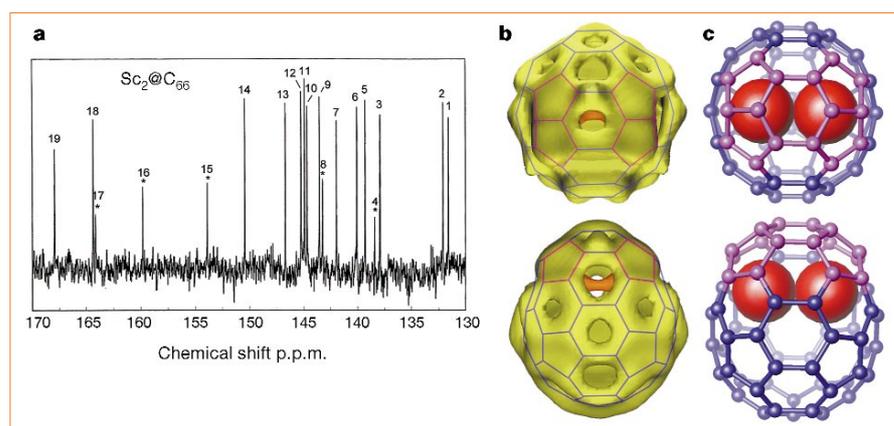
Figure 1 ^{13}C NMR and synchrotron X-ray powder diffraction structural data on $Sc_2@C_{66}$. **a,** ^{13}C NMR spectrum of $Sc_2@C_{66}$ in CS_2 solution (2.5 mg Cr(acac)₃, where 'acac' represents acetylacetonate, relaxant and C_6D_6 lock) after 160,000 scans at room temperature using a Varian Inova 600 spectrometer at 600 MHz. The five lines marked with an asterisk are half the intensity of the other 14 full lines (131.6, 132.1, 137.9, 138.4*, 139.3, 140.1, 142.0, 143.3*, 143.5, 144.7, 144.9, 145.2, 146.7, 150.4, 153.9*, 159.8*, 164.1*, 164.4 and 167.9 p.p.m.). **b,** X-ray structure of the IPR-violating $Sc_2@C_{66}$ fullerene, showing a top view along the C_2 axis and a side view. The equi-contour (1.4 e Å^{-3}) surface of the final maximum-entropy method electron charge density is shown; the Sc_2 dimer is in red and the two pairs of fused pentagons are evident. The X-ray powder pattern had good counting statistics and was measured in an X-ray powder experiment using synchrotron radiation and imaging-plate detectors exposed for 2 h (incident X-ray wavelength, 0.75 Å). The X-ray powder pattern of $Sc_2@C_{66}$ was obtained with a 0.02° step up to 20.3° in 2θ, which corresponds to 2.0 Å resolution in d spacing. **c,** Calculated $Sc_2@C_{66}$ structures (see text).

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Materials science

# A stable non-classical metallofullerene family

In the evolving field of fullerenes, nanotubes and endohedral metallofullerenes, the isolated-pentagon rule (IPR)[1] is sacrosanct — exceptions have been predicted[2,3], but no bare carbon cages with adjacent pentagons have been characterized. Small organic molecules with metal-stabilized fused five-membered rings (pentalenes) have been created[4], however, and here we describe a family of non-classical endohedral metallofullerenes with the general structure $A_xSc_{3-x}N@C_{68}$ (where $x=0$–2, A is a rare-earth metal, Sc is scandium and N is nitrogen) that has a non-IPR cage of only 68 carbon atoms containing annelated five-membered rings. This internal ring network is metal-stabilized and is accessible for external organic reaction chemistry.

We formed the scandium encapsulate $Sc_3N@C_{68}$ in a Krätschmer–Huffman[5] generator using the trimetallic nitride template (TNT, in the presence of nitrogen) process, purifying the encapsulate by chromatography[6]. We obtained $Sc_3N@C_{68}$ (Fig. 1a) with soluble extract yields of 1–2%; this is better than the most abundant non-TNT scandium encapsulate, $Sc_2@C_{84}$, and is only exceeded by the $Sc_3N@C_{80}$ family.

It is easy to prepare other non-IPR family members, $A_xSc_{3-x}N@C_{68}$ ($x=0$–2) from graphite rods containing a mixture of scandium and rare-earth metal (A) oxide[6], as our chromatographic isolation of a purified sample of $ErSc_2N@C_{68}$ at levels similar to $Sc_3N@C_{68}$ shows (Fig. 1b). Yields of this mixed scandium/rare-earth family for $ASc_2N@C_{68}$ and $A_2ScN@C_{68}$, where A can
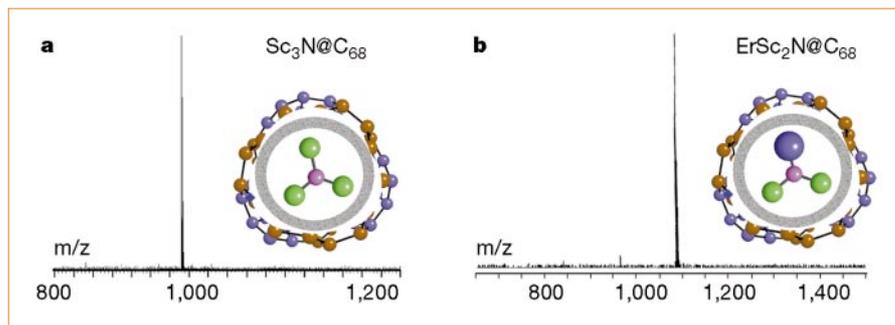
Figure 1 Mass-spectral data for purified $Sc_3N@C_{68}$ and $ErSc_2@C_{68}$. **a,** The NI-DCI mass spectrum for $Sc_3N@C_{68}$, with $m+1$, $m+2$ and $m+3$ isotope intensities have predicted (observed) values of 76.70 (76.8 ± 2.2), 28.98 (28.0 ± 1.2) and 7.19 (7.6 ± 0.5), respectively. **b,** The NI-DCI mass spectrum for purified $ErSc_2@C_{68}$, with m, $m+1$, $m+2$ and $m+3$, have predicted (observed) isotope intensities of 63.3 (62.2 ± 4.8), 90.3 (84.2 ± 8.5), 100 (100) and 54.4 (53.0 ± 4.2), respectively. The 150-MHz ^{13}C-NMR spectrum for $Sc_3N@C_{68}$ consists of signals at 158.49, 150.40, 149.51, 147.41, 145.52, 143.55, 142.92, 137.77, 137.62, 137.19, 137.12 and 136.87 (1/3 intensity) p.p.m. The ^{45}Sc and ^{13}C NMR, UV–visible, and chromatographic data for $Sc_3N@C_{68}$ are given in Supplementary Information.
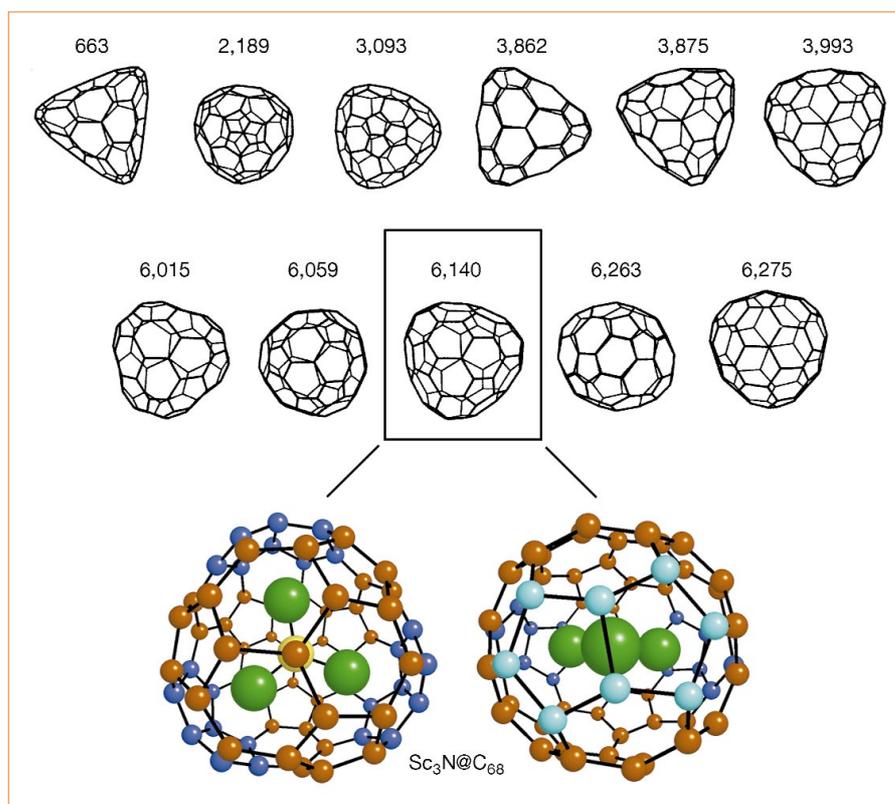
Figure 2 Three-fold symmetry isomers of C_{68} and proposed $Sc_3N@C_{68}$ structure (isomer 6,140). There are 11 non-IPR isomers generated from the spiral algorithm[7] with three-fold symmetry axis consistent with 12 ^{13}C NMR lines (11 of equal intensity and 1 of one-third intensity) and a single symmetric ^{45}Sc NMR signal. Isomer 663, D_3, $N_p=15$; isomers 2,189, 3,093, 3,862, 3,875 and 3,993, D_3, $N_p=9$; isomers 6,015 and 6,059, D_3, $N_p=6$; isomer 6,263, S_6, $N_p=6$; isomers 6,140 and 6,275, D_3, $N_p=3$. Isomer 6,140 has spiral $5^2 6^6$ $(56)^2 6 (56)^2 6^4 5 6^4 (56)^5$. Two orthogonal views are shown for the proposed $Sc_3N@C_{68}$ structure generated from isomer 6,140 geometry (DFTB computation level) with encapsulation of the Sc_3N cluster. Views are shown from the C_3 axis and the C_2 axis.

be Tm, Er, Gd, Ho or La, were more modest (see Supplementary Information). The absence of measurable quantities of endohedral clusters of three larger rare-earth atom clusters ($A_3N@C_{68}$) is consistent with the much larger radii of rare-earth atoms compared with Sc ions in a space-confining cage of only 68 carbon atoms.

For fullerenes smaller than C_{70}, only C_{60}, with its classic icosahedral cage, has an isomer allowed by the IPR[1]. For a C_{68} cage, the spiral algorithm[7] finds 6,332 distinct

fullerenes containing pentagon and hexagon rings, but only 11 of these structures are consistent with the single symmetric line and 12 singlet peaks (11 of equal intensity and 1 of one-third intensity) seen in the ^{45}Sc and ^{13}C NMR spectra, respectively, for $Sc_3N@C_{68}$ (see Supplementary Information). All candidate isomers have either D_3 or S_6 symmetry (Fig. 2). From the NMR data and assuming three-fold symmetry, other defect rings, such as heptagons, in alternative cages would have to occur in sets