The stabilization of fused-pentagon fullerene molecules

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The isolated pentagon rule (IPR) is now widely accepted as a general rule for determining the stability of all-carbon fullerene cages composed of hexagons and pentagons. Fullerenes that violate this rule have been deemed too reactive to be synthesized. The stabilization of non-IPR endohedral fullerenes depends on charge transfer from the encapsulated metal clusters (endoclusters) to fullerene cages, the electronic properties of empty all-carbon cages, the matching size and geometries of fullerene and endocluster, as well as the strong coordination of the metal ions to fused pentagons. The stability of non-IPR exohedral fullerenes can be rationalized primarily by both the 'strain-relief' and 'local-aromaticity' principles. This Review focuses on recent work on stabilization of non-IPR fullerenes, including theoretical and empirical principles, experimental methods, and molecular structures of fused-pentagon fullerenes characterized so far. The special chemical properties of non-IPR fullerenes that distinguish them from IPR-satisfying ones are also emphasized.

he remarkable discovery that C_{60}^{+} is unusually stable among the carbon cluster ions produced by laser vaporization of graphite was reported by Kroto, Heath, O'Brien, Curl and Smalley in 1985¹. They hypothesized that this stability resulted from its truncated icosahedron cage structure and dubbed this C_{60} molecule 'buckminsterfullerene' after the eponymous architect, Buckminster Fuller. Soon after the discovery, they realized that the soccer-ball-structured buckminsterfullerene was just one member in the huge family of all-carbon clusters having a hollow cavity. Note that the concept of cage-shaped all-carbon molecules can be dated back to 1966 when Daedalus, alias D. E. H. Jones², suggested the possibility of making giant fullerenes, and to 1970 when Osawa³ proposed the spherical I_h-symmetric football structure with 60 carbon atoms. The IUPAC nomenclature for naming the cage structure is too complicated for general use and this whole family is classically called fullerenes, fulfilling Euler's Theorem. Taking only pentagons and hexagons into account, the classical fullerenes are closed-cage C_n clusters having an even number ($n \ge 20$ with the exception of n = 22) of carbons at three-connected vertices, 3n/2 C–C edges, (n-20)/2 hexagons and 12 carbon pentagons. Topologically the number of fullerene isomers is enormous. If non-classical fullerenes incorporating heptagons or tetragons are considered, the number of isomers is significantly more.

However, only a tiny fraction of them can survive in air. The most notable are I_{h} -^{#1,812} C_{60} and D_{5h} -^{#8,149} C_{70} (the nomenclature is specified by symmetry or/and by spiral algorithm to differentiate the isomers⁴). To understand the special stability of I_{h} -^{#1,812} C_{60} and D_{5h} -^{#8,149} C_{70} that sets them apart from the high reactivity of other carbon clusters with presumed fused-pentagon structures, Kroto⁵ proposed that all stable fullerenes have pentagons isolated by hexagons, and the presence of pentagon-fusions (Fig. 1) results in enhanced local strain and reduced stability. Supported by experimental and theoretical evidence, Kroto's proposal has now been well-recognized and widely adopted as the isolated pentagon rule (IPR) for determining the stability of fullerene cages composed of hexagons and pentagons. Outside the gas phase, all the fullerene molecules synthesized so far strictly obey this rule.

The destabilization of non-IPR fullerenes was explained by Kroto to result from an increase of local steric strain caused by fused pentagons⁵. This steric effect is increased with the increasing number of adjacent pentagons as shown in Fig. 1. Note that the simplest unit of fused pentagons, that is, pentalene itself, is a highly reactive species that was proposed⁶ in 1922 and finally isolated⁷ in 1997. Schmalz and colleagues explained that adjacent pentagons had 'eight-cycle'-type 8π -electron substructures in violation of Hückel's (4n+2) rule, thus leading to resonance destabilization^{8,9}. Moreover, π -orbital overlap is also reduced generally due to cage curvature caused by adjacent pentagons^{10,11}. Very recently, a headto-tail exclusion rule has been proposed as the basis for the IPR in fullerenes having more than 60 vertices¹².

Table 1 lists the isomer numbers of IPR-satisfying and non-IPR types of selected fullerenes⁴. It shows that the number of non-IPR fullerene isomers is much larger than that of IPR-satisfying ones for a given cluster size. Nonetheless, fullerene research has overwhelmingly focused on C_{60} and C_{70} . This is simply because of their significant stability. According to Euler's Theorem, the smallest IPR-satisfying fullerene is I_h - C_{60} , immediately followed by D_{5h} - C_{70} . The huge number of 'missing' non-IPR fullerenes challenges chemists to bring them into reality. Over the past ten years, significant advances have been achieved in stabilizing and isolating these labile fullerenes by exohedral derivatization, by endohedral encapsulation of electron-donating metal atoms or clusters, or by combinations thereof.



Figure 1 | Basic fused-pentagon configurations (with 2-3 pentagon subunits) in non-IPR fullerenes. a, Double fused pentagons. b, Triple sequentially fused pentagons. c, Triple directly fused pentagons. Note that this set can be extended to multiple configurations with four or more pentagon subunits.

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This Review focuses on the stabilization of non-IPR fullerenes, including theoretical and empirical principles, experimental methods, and molecular structures of non-IPR fullerenes thus obtained. Properties of non-IPR fullerenes have been less reported because of their experimental scarcity, though theoretical studies have been carried out for many years and have been reviewed recently¹³. The special chemical reactivity and regioselectivity of fused-pentagon fullerenes that differ from those of IPR-satisfying ones are emphasized in this article. In addition to the non-IPR fullerenes having only pentagons and hexagons, two cases of heptagon- and tetragonincorporating non-classical fullerenes are briefly mentioned; other labile fullerenes (such as low-bandgap IPR fullerenes and heterofullerenes) are not considered here.

Non-IPR fullerenes stabilized by endohedral derivatization

One of the most distinct features of fullerenes is their cage configuration. It can accommodate reactive atoms or clusters in the interior cavity. Shortly after the initial discovery of buckminsterfullerene¹, evidence for an endohedral lanthanum complex of C_{60} was observed in mass spectrometry by Smalley and co-workers¹⁴. This complex was notated as La@C₆₀, where the symbol @ is used to define the left-marked atoms encapsulated in the interior of the right-indicated fullerene. This special symbolism has been widely accepted, but it is different from the IUPAC nomenclature, by which M@C_n is named [n]fullerene-*incar*-metal and should be written as iMC_n .

Several excellent articles have reviewed recent research on endofullerenes¹⁵⁻¹⁸. Different endoclusters have been found within the endofullerenes: metal clusters, metal nitrides, metal carbides and metal oxides. The endofullerenes containing a single metal atom or multimetal cluster are also conventionally called metallofullerenes. It has been demonstrated that group 2 (M = Ca, Sr, Ba) and group 3 metals (M = Sc, Y) and most lanthanides can be trapped inside fullerenes to form stable endofullerenes. The most widely investigated endofullerenes are those encapsulating trimetallic nitrides.

Theoretical papers in the early 1990s proposed that labile non-IPR fullerenes might be stabilized by intramolecular electron transfer from the endocluster to the fullerene cage¹⁸. Practical synthesis and structural identification of non-IPR endohedral fullerenes, however, were not successful until 2000 when two independent groups led by Shinohara and Dorn reported two kinds of non-IPR endohedral fullerene, $Sc_2@^{#4,348}C_{66}$ (ref. 19) and $Sc_3N@^{#6,140}C_{68}$ (ref. 20), respectively.

The principles for endohedral stabilization of non-IPR fullerenes. It is very interesting to see that the carbon cages found in endofullerenes, often different from the empty fullerenes isolated so far, are produced only when they are negatively charged from the encapsulated species. Accordingly, the stabilization of the endofullerene seems to relate to the ionic fullerene negative charge from the encapsulated species irrespective of the stability of the neutral cage itself. Poblet and colleagues²¹ proposed a simple rule for predicting the most suitable cage isomers capable of encapsulating nitride clusters. This rule states that, for example, in the case of $Sc_3N@^{#6,140}C_{68}$ (refs 20–22; Fig. 2), a suitable fullerene host for encaging a trimetallic nitride should have a sizeable (LUMO-3)-(LUMO-4) gap and achievable energies. This rule is based on the assumption that a total of six electrons formally transfer from the three highest occupied molecular orbitals (HOMOs) of the trimetallic nitride to three low-lying unoccupied molecular orbitals (LUMOs) of the cage. Although the calculated molecular orbital (MO) levels of C_{68}^{6-} are not completely the same as that of $Sc_3N@$ C_{68} (Fig. 2), the HOMO–LUMO gap of the resulting $Sc_3N@^{\#6,140}C_{68}$, formally described as the ionic model $Sc_3N^{6+}@^{\#6,140}C_{68}^{6-}$, could be estimated from the (LUMO-3)-(LUMO-4) gap of the free neutral cage as shown in Fig. 2. Screening through a large number of IPR and non-IPR (with fewer than four adjacent pentagons) fullerene

Table 1 The numbers of IPR-satisfying or non-IPR fu	llerene
isomers C_n ranging from C_{20} to C_{100} .	

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n	Non-IPR	IPR	n	Non-IPR	IPR
20	1	0	62	2,385	0
24	1	0	64	3,465	0
26	1	0	66	4,478	0
28	2	0	68	6,332	0
30	3	0	70	8,148	1
32	6	0	72	11,189	1
34	6	0	74	14,245	1
36	15	0	76	19,149	2
38	17	0	78	24,104	5
40	40	0	80	31,917	7
42	45	0	82	39,710	9
44	89	0	84	51,568	24
46	116	0	86	63,742	19
48	199	0	88	81,703	35
50	271	0	90	99,872	46
52	437	0	92	126,323	86
54	580	0	94	153,359	134
56	924	0	96	191,652	187
58	1,205	0	98	230,758	259
60	1,811	1	100	285,463	450

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isomers with density functional theory (DFT) calculations, Popov and Dunsch²³ have predicted the most stable $M_3N@C_n$ for a broad range of fullerenes (C_{68} to C_{98}). They found that up to a cage size of C_{84} , non-IPR isomers of C_n^{6-} and $M_3N@C_n$ are comparable to or even more stable than IPR isomers.

Poblet's rule is also applicable for endofullerenes having a single/multimetal or metallic carbide endocluster. The interior clusters will transfer a number of electrons to the fullerene depending on the electronic properties of the metal cluster itself. For example, two electrons are transferred in $Ca@C_n$ from Ca to the C_n cage²⁴,





whereas four electrons are transferred for trivalent metallic carbide M_2C_2 clusters where the C_2 moiety is a dianion^{25,26}. So the stability for Ca@C_n depends on a large (LUMO-1)–(LUMO-2) gap, whereas trivalent metallic carbide endofullerenes rely on the large (LUMO-2)–(LUMO-3) gap of the free fullerenes.

Poblet's rule is based on first principles without consideration of cage symmetry or geometry. The geometric structure of endofullerenes is, however, another factor governing their stability. First, a fullerene cage with too small a cavity is not suitable in principle for encapsulating big clusters. For example, there is no evidence to support the encapsulation of a trimetallic nitride by C₆₀, although C₆₀ has a (LUMO-3)-(LUMO-4) gap of more than 1 eV that satisfies Poblet's rule. At present, the smallest cage to encapsulate an M₃N cluster is C₆₈. Second, the geometries of both fullerenes and interior clusters can be deformed as a result of the mutual interaction. Thus, the normally pyramidal trimetallic nitrides typically become a planar cluster inside the fullerene cage (with an exception for Gd₃N@C₈₀, for which the Gd₃N cluster is pyramidal with the nitrogen atom displaced about 0.5 Å out of the Gd₃ plane²⁷). Moreover, the interaction between endocluster and fullerene is such that the type of fullerene cage can be sorted by endocluster. For example, whereas the Sc₃N cluster is planar in an IPR-satisfying Sc₃N@^{#24,109}C₇₈ endofullerene²⁸, the relatively large Y₃N and Lu₃N clusters would be forced to be pyramidal inside this IPR-cage, which would result in their destabilization. Instead, these clusters remain planar in the non-IPR #22,010C78 isomer, making Y₃N@^{#22,010}C₇₈ and Lu₃N@^{#22,010}C₇₈ the most stable endofullerenes with this C_{78} cage structure²⁹.

The mechanism of non-IPR fullerene stabilization is seen to be analogous to that operative in IPR-satisfying fullerenes, but the existence of fused pentagons facilitates electron transfer and coordinate-bonding interactions between metals and cage carbon atoms at pentagon fusions. In contrast to many IPR-satisfying endofullerenes (such as $La_2@^{\pm31,924}C_{80}$, ref. 30; $Sc_3N@^{\pm31,924}C_{80}$, ref. 31) featuring motion of encapsulated clusters, non-IPR endofullerenes show strong coordination of the metal atoms to the fused pentagons. The cases of $Sc_3N@^{\pm7,854}C_{70}$ (ref. 32) and $DySc_2N@^{\pm17,490}C_{76}$ (ref. 33) show that the magnitude of the coordinate-bonding interaction is so strong that the N–M–N bond angles deviate from 120° to fit the positions of the fused pentagons. This can be compared to many data for the strong coordination of organometallic groups to the inner face of pentalene and substituted pentalenes³⁴.

Briefly, the stabilization of non-IPR endohedral fullerenes depends in principle on the following factors. (1) Charge transfer from the encapsulated metal cluster (endocluster) to the fullerene cage. (2) Electronic properties of the empty fullerene cage. (3) The matching size and geometries of the fullerene and the endocluster. (4) Strong coordination of the metal ions to the fused pentagons.

Strategy for synthesis, isolation and identification of non-IPR endohedral fullerenes. The production of endofullerene in a detectable amount was first accomplished by pulsed laser vaporization of a lanthanum oxide–graphite composite rod in a flow of argon gas (100–200 torr) at 1,200 °C (ref. 35). Owing to low yields, however, the laser-vaporization method is now rarely used for the production of endofullerenes.

Arc-discharge was the initial breakthrough method for the macroscopic synthesis of C_{60} reported by Kräschmer and Huffman³⁶ in 1990. It is still the most routinely used method for preparing macroscopic amounts of endohedral fullerenes. The yield of target endofullerenes is normally low and is sensitive to reaction conditions. By introducing reactive NH₃ gas into the Kräschmer–Huffman generator during the vaporization of a graphite composite, typically impregnated with various metal oxides or carbides, the quantity of endofullerenes encapsulating metal nitride clusters, such as $Sc_3N@^{#6,140}C_{68}$ and $Dy_3N@C_n$ ($78 \le n \le 88$), has been reported as dominant products in the soot extraction^{22,37}. Another example is that the yield of $La@C_{82}$ increases by a factor of ten when composite graphite rods with metal carbide, produced from a high-temperature (above 1,600 °C) annealing of metal oxide, are used to generate soot³⁸.

To obtain pure endofullerenes from the product mixture, highperformance liquid chromatography (HPLC) is a routine isolation technique. Because of the similar chromatographic behaviour of endofullerenes, however, preparative isolation of endofullerenes in macroscopic quantities has been very difficult and time-consuming. It took almost two years after the first extraction of $La@C_{82}$ for metallofullerenes to be completely isolated by HPLC^{35,39}. Furthermore, the solubility of endofullerenes in ordinary HPLC solvents is normally low. The multistage recycling HPLC method has been adopted for efficient isolation of fullerenes with similar chromatographic behaviour, through re-feeding the eluted components back to columns for repeated HPLC runs.

Chemical methods have also been reported for endofullerene isolation, typically coupled to HPLC. Both selective chemical oxidation⁴⁰ and electrochemical reduction⁴¹ have been used, depending on the solubility changes resulting from chemical modification of endofullerenes. Furthermore, a simple separation of two isomers of $Sc_3N@^{#31,924}C_{80}$ (I_h) and $Sc_3N@^{#31,923}C_{80}$ (D_{5h}) has recently been conducted by Echegoyen and colleagues on the basis of a selective chemical oxidation of the D_{5h} isomer⁴². For the isolation of trimetallic nitride endofullerenes such as $Sc_3N@C_{68}$, $Sc_3N@C_{78}$ and $Sc_3N@C_{80}$ from empty fullerenes, the selective binding of empty cage fullerenes to cyclopentadiene-functionalized styrene-divinylbenzene resin⁴³

	Synthesis conditions		Number of doubly	Charge transfer	
	Graphite composite	Atmosphere	fused pentagons	from the endocluster	Ref.
Sc ₂ @ ^{#4,348} C ₆₆	Scandium and rare-earth metal/graphite	He	2	2	19
$Sc_3N@^{\#6,140}C_{68}$	Scandium oxide/graphite	He/N_2	3	6	20, 53
Sc ₂ C ₂ @ ^{#6,073} C ₆₈	Scandium/graphite carbide	He	2	4	25
Sc ₃ N@ ^{#7,854} C ₇₀	Scandium/graphite	He/NH ₃	3	6	32
La@ ^{#10,612} C ₇₂	Lanthanum/graphite	He	1	3	58
La2@#10,611C72	Lanthanum/graphite	He	2	6	59,61,62
DySc ₂ N@ ^{#17,490} C ₇₆	Dysprosium and scandium oxide/graphite	He/NH ₃	2	6	33
Dy ₃ N@ ^{#22,010} C ₇ 8	Dysprosium oxide/graphite	He/NH_3	2	6	37,64
$Gd_3N@^{\#39,663}C_{82}$	Gadolinium oxide/graphite	He/N_2	1	6	65
$M_{3}N@^{\#51,365}C_{84}$	Metal oxide/Fe _x N/graphite	He/N ₂	1	6	66,67
(M = Gd Th Tm)					

Table 2 | Non-IPR endohedral fullerenes synthesized and characterized.



Figure 3 | Structures of metallofullerenes. a, $\mathsf{Sc}_2 @^{\#4,348}\mathsf{C}_{66}$

b, La@^{#10,612}C₇₂(C₆H₃Cl₂). **c**, La₂@^{#10,611}C₇₂. Scandium and lanthanum are indicated as magenta and cyan spheres respectively (at 100% van der Waals radius). The fused pentagons in each fullerene are highlighted in red. Parts **a**, **b** and **c** reprinted from, respectively, ref. 19, © 2000 NPG; ref. 58, © 2006 ACS; ref. 59, © 2003 ACS.

or to amino-capped silica gel⁴⁴ were performed. A solvent-free reaction in molten 9-methylanthracene was also used for isolation of trimetallic nitride endofullerenes from the crude soot extract⁴⁵. The principle for these chemical separation methods is based on the reactivity difference between empty fullerenes and endofullerenes: free empty-cage fullerenes are electron deficient and therefore are fairly reactive, whereas the endofullerenes are stabilized by electron transfer from the endoclusters, resulting in lower reactivity.

Synchrotron X-ray diffraction was used early in the structural identification of non-IPR endofullerenes¹⁹. Experimental data were analysed in an iterative way using a combination of Rietveld analysis⁴⁶ and maximum entropy (MEM)⁴⁷, though its reliability actually depends on the structural model chosen in the Rietveld analysis. The story of Sc₃@C₈₂ versus Sc₃C₂@C₈₀ is an example of this issue. Takata *et al.*⁴⁸ first characterized the Sc₃@C₈₂ structure by synchrotron X-ray diffraction in 1999, but later crystallographic data by Akasaka and Nagase²⁶ in 2005 redefined this structure as Sc₃C₂@C₈₀. Density functional theory calculations by Tan and Lu⁴⁹ corroborated the structure of metal-carbide endofullerene Sc₃C₂@C₈₀ having the valence state (Sc³⁺)₃(C₂)³⁻@C₈₀⁶⁻. Starting from the identified molecular model, Nishibori and co-workers⁵⁰ using the MEM/ Rietveld method finally refined the structure as Sc₃C₂@C₈₀.

Nuclear magnetic resonance spectroscopy is a commonly used technique for structure determination of endofullerenes in combination with theoretical computation. However, the usually low symmetry of endofullerenes can lead to complex and unassignable NMR spectra. Thus X-ray crystallography is more powerful for determining molecular structure. However, bare spherical structures for endofullerenes usually result in unavoidable cage disorder in the crystal. Exohedral derivatization by chemical groups or intermolecular interactions with M(OEP)s (M = metal, OEP = 2,3,7,8,12,13,17,18-octaethylporphinate) is thus necessary to order endofullerene cages in the crystal. In the absence of X-ray crystallographic data, DFT computations coupled to spectroscopic

data (such as optical bandgap and vibrational spectra) may be considered an alternative for the characterization of the most stable endofullerene isomers.

Non-IPR endohedral fullerenes synthesized and characterized. In 2000, two different groups sequentially published their independent work on the endohedral non-IPR fullerenes $Sc_2@^{#4,348}C_{66}$ (ref. 19) and $Sc_3N@^{#6,140}C_{68}$ (ref. 20). Both are fullerenes between C_{60} and C_{70} , and thus by Euler's Theorem cannot obey the IPR. Since this pioneering work, several endofullerenes have been synthesized, typically in a Kräschmer–Huffman arc-discharge process and identified in the form of non-IPR fullerenes encapsulating metals, metal nitrides or metal carbides (Table 2). All the fused pentagons in the already identified non-IPR endofullerenes are of the class of double fused pentagons.

 C_{66} endofullerene. Based on the 19-line ¹³C NMR spectrum and synchrotron X-ray powder-diffraction data, the Sc₂@ C_{66} isolated by Shinohara and co-workers¹⁹ was identified as being the C_{2v} symmetric ^{#4,348}C₆₆ non-IPR cage encapsulating a Sc₂ dimer close to the fused pentagons (Fig. 3a). However, DFT calculations by Kobayashi and Nagase⁵¹ predicted a more energetically favoured C_{2v} Sc₂@^{#4,059}C₆₆ to fit the observed 19-line ¹³C NMR spectrum. This structure contains two pairs of triple sequentially fused pentagons and two separated Sc atoms. Later, Takata and co-workers⁵² used high-resolution synchrotron radiation powder data in combination with the MEM/ Rietveld method to re-determine the structure as Sc₂@^{#4348}C₆₆ with the covalent bonded Sc₂ dimer.

 C_{68} endofullerene. The A_xSc_{3-x}N@C₆₈ family was synthesized by Dorn and colleagues from arc-discharge of graphite rods containing a mixture of scandium and rare-earth metal (A = Tm, Er, Gd, Ho or La) oxide in the presence of nitrogen²⁰. From an NMR spectrum with a single symmetric ⁴⁵Sc line and 12 singlet ¹³C peaks (11 of unit intensity and 1 of one-third intensity), one of the purified products was characterized as Sc₃N@#6,140C₆₈ (Fig. 4a). The structure consisting of an encapsulated Sc₃N cluster in a $^{\#6,140}C_{68}(D_3)$ cage was further confirmed three years later by the same group using X-ray crystallography⁵³. The geometric structure shows that the scandium atoms are situated over the centres of pentalene portions inside the fullerene cage. The short metal-to-carbon distances (2.225(5)-2.450(5) Å) involve the carbon atoms at the pentagon-pentagon junctions, implying coordination of the scandium atoms to the pentalene portion to stabilize the endofullerene structure. The π -orbital axis vector (POAV) pyramidalization angle⁵⁴ of the carbon atoms at



Figure 4 | Structures of trimetallic nitride endofullerenes. a, $Sc_3N(@^{#6140}C_{68}$. b, $Sc_3N(@^{#7,854}C_{70}$. c, $DySc_3N(@^{#17,490}C_{76}$. d, $M_3N(@^{#22,010}C_{78}$ (M = Dy, Tm) represented by $Dy_3N(@^{#22,010}C_{78}$. e, $Gd_3N(@^{#39,663}C_{82}$. f, $M_3N(@^{#51,365}C_{84}$ (M = Gd, Tb, Tm) represented by $Gd_3N(@^{#51,365}C_{84}$. Fused pentagons are highlighted in red. Parts **a-f** adapted from, respectively, ref. 20, © 2000 NPG; ref. 32, © 2007 Wiley; ref. 33, © 2007 ACS; ref. 29, © 2007 ACS; ref. 65, ©2008 ACS; ref. 66, © 2006 ACS.



Figure 5 | Structure of Sc_2C_2 ^{(m *6,073} C_{68} with metal carbide inside. Fused pentagons are highlighted in red. Reprinted from ref. 25, © 2006 Wiley.

the pentagon fusion is significantly higher (16.5°) than it is for the other carbon atoms of the cage $(8.8-12.2^{\circ})$.

Wang, Lu and Shinohara²⁵ reported the characterization of another non-IPR C₆₈ cage stabilized by metal carbides. The 21-line ¹³C NMR spectrum, supported by theoretical computations, indicates that its carbon cage is ^{#6,073}C₆₈ and the encpsulated group is a di-scandium acetylide (Fig. 5). The difference between the C₆₈ cages in Sc₂C₂@^{#6,073}C₆₈ and Sc₃N@^{#6,140}C₆₈ is noteworthy as it results from the different endoclusters, exemplifying that endoclusters can act as a template to modulate the type of fullerene cage.

 C_{70} endofullerene. From the products of scandium/graphite arc-discharge in NH₃, Yang, Popov and Dunsch³² isolated a further endofullerene species, Sc₃N@C₇₀. The IPR-obeying D_{5h} -^{#8,149}C₇₀ was originally considered as the structure of the isolated species. However, this possibility for the Sc₃N@^{#8,149}C₇₀ structure was ruled out because of the difference between experimental data and computation for both the infrared spectrum and the HOMO–LUMO gap. Screening through 116 C₇₀ isomeric sixfold-charged anions with three or fewer pairs of fused pentagons, the ^{#7,854}C₇₀⁶⁻ has exclusively a large HOMO–LUMO gap (1.23 eV) and high stability. Therefore, the most probable non-IPR structure of Sc₃N@^{#7,854}C₇₀ (Fig. 4b) was assigned by the authors³².

 C_{72} endofullerene. The original computational studies conducted by Nagase and Kobayashi in 1997 suggested that the endofullerenes of Ca@C₇₂ might have non-IPR structures⁵⁵. In experiment, two isomers of Ca@C₇₂ were isolated from the soot arc-discharge of calcium/graphite composite rods^{56,57}. As there is only one IPR isomer possible for C₇₂, the existence of two isomers of Ca@C₇₂ indicates that at least one must have a non-IPR structure if the isomerization comes from the cage and not from the location of the metal inside the cage. However, no conclusive evidence for the structural identification was obtained until 2006, when Akasaka and colleagues⁵⁸ obtained crystals of La@C₇₂ from the 1,2,4-trichlorobenzene-extraction of the lanthanum/graphite arc-discharge soot. The non-IPR cage of ^{#10,612}C₇₂ in the form of La@^{#10,612}C₇₂(C₆H₃Cl₂) was identified by X-ray crystallography. The encapsulated La atom was found to be located in the fold of the fused pentagons (Fig. 3b).

Another representative C_{72} cage that has been stabilized is $^{\pm 10.611}C_{72}$. Shinohara and co-workers⁵⁹ reported the initial isolation and ^{13}C NMR spectroscopic characterization of La₂@C₇₂ from the soot of lanthanum/graphite arc-discharge. Based on the 18-line ^{13}C NMR spectrum, either $^{\pm 10.611}C_{72}$ or $^{\pm 10.958}C_{72}$ non-IPR cage structure were proposed⁵⁹, whereas theoretical calculations⁶⁰ suggested that the La₂@ $^{\pm 10.611}C_{72}$ should be more stable. Recently, the structure of La₂@ $^{\pm 10.611}C_{72}$ (Fig. 3c) has been confirmed by Akasaka and Nagase^{61,62} by way of a crystalline exohedral derivative obtained in photolytic reaction with the carbene reagent 2-adamantane-2,3-[3H]-diazirine.

Recently, *10.611C₇₂ has been ¹³C NMR spectroscopically and computationally confirmed to also be able to encapsulate two Ce atoms⁶³.

 C_{76} endofullerene. Ultraviolet–visible near-infrared spectroscopy shows the absorption spectral onset at ~1,300 nm for DySc₂N@C₇₆ (ref. 33), indicating an optical bandgap of 0.96 eV. Fullerene C₇₆ has two isomers (^{#19,150}C₇₆ and ^{#19,151}C₇₆) that obey the IPR, but they are excluded from possible candidates because of their smaller HOMO–LUMO gap (0.75 and 0.14 eV for ^{#19,150}C₇₆ and ^{#19,151}C₇₆, respectively) for sixfold-charged anions. Screening C₇₆^{6–} anions on the basis of the lowest energy and the HOMO–LUMO gap comparable to experimental observation, the fullerene cage of DySc₂N@C₇₆ was suggested to be ^{#17,490}C₇₆ having two pairs of adjacent pentagons³³.

There are two typical orientations for the endocluster DySc₂N inside the ^{#17,490}C₇₆ cage: one is such that the two Sc atoms are perpendicular to two pairs of fused pentagons, respectively; a second is as shown in Fig. 4c. A comparison of DFT-simulated infrared spectra of these two regioisomers with experimental data suggested the DySc₂N@^{#17,490}C₇₆ structure shown in Fig. 4c. Dunsch and co-workers³³ explained the stability of DySc₂N@^{#17,490}C₇₆ through rationalization of the endocluster geometries of Sc₃N@^{#17,490}C₇₆, Y₃N@^{#17,490}C₇₆ and YSc₂N@^{#17,490}C₇₆, for which Y might be replaced by Dy. As the asymmetric YSc₂N cluster has a more suitable geometry for the inner space of the ^{#17,490}C₇₆ cage than those of the homogeneous clusters like Sc₃N or Y₃N, the highest yield for ^{#17,490}C₇₆-based endofullerenes with Dy_xSc_{3-x}N (x = 0-3) cluster is achieved experimentally for the DySc₂N@^{#17,490}C₇₆.

 C_{78} endofullerene. Computation-optimized structural data of $M_3N@C_{78}$ (M = Sc, Tm, Dy) demonstrated that the fullerene isomers can be defined by the size of the endoclusters. Sc₃N@C₇₈ has a cage structure of the IPR fullerene D_{3h} -^{#24,109}C₇₈ (ref. 28). X-ray or ¹³C NMR spectroscopic data are not yet available for Tm₃N@C₇₈ and Dy₃N@C₇₈^{37,64}, but Popov and Dunsch²⁹ have characterized them by infrared and Raman vibrational spectroscopies and DFT computation as the non-IPR $C_2^{+22,010}C_{78}$ cage structure (Fig. 4d). The most stable C₇₈⁶⁻, identified by semi-empirical calculations and DFT optimization of C₇₈ hexa-anions, is $^{\#24,109}C_{78}$, followed by $^{\#22,010}C_{78}$ and $^{#24,107}C_{78}$. Further DFT calculations for a series of M₃N@C₇₈ (M = Sc, Y, Lu, La) isomers showed that the stability order of the isomers dramatically changes depending on the cluster size. These changes in relative stability can be rationalized on the basis of the structures of the encapsulated clusters. For example, whereas Sc₃N is planar in $^{#24,109}C_{78}$, the limited space in this cage forces larger clusters to be pyramidal. On the other hand, in the lowest-energy non-IPR isomer (#22,010), the cavity is large enough to accommodate Y₃N and Lu₃N clusters in a nearly planar or strictly planar geometry, resulting in the stable endofullerenes $Y_3N@^{\#22,010}C_{78}$ and $Lu_3N@^{\#22,010}C_{78}$.

 C_{82} endofullerene. The structures $M_3N@^{\pm 39,705}C_{82}$ and $M_3N@^{\pm 39,663}C_{82}$, having a pentagon fusion, were suggested to be the most probable isomers for $M_3N@C_{82}$ (ref. 23). X-ray crystallographic studies by Balch, Echegoyen, Olmstead and colleagues⁶⁵ have now confirmed one of them as $Gd_3N@^{\pm 39,663}C_{82}$ (Fig. 4e). In the crystal obtained by diffusion of the endohedral fullerene into Ni^{II}(OEP) benzene solution, the egg-shaped $Gd_3N@^{\pm 39,663}C_{82}$ molecule is nestled within the eight ethyl groups of the Ni^{II}(OEP) molecule, showing the importance of Ni^{II}(OEP) for fixing the fullerene cage. The structure shows disorder for the Gd atom and carbon cage. The Gd₃N cluster is planar with a 359.6° sum for the three Gd–N–Gd angles. A Gd atom is situated within the fold of the adjacent pentagons, with short Gd–C distances in the range of 2.476(10) to 2.554(10) Å.

 C_{84} endofullerene. Theoretical computations²³ suggested that C_{84} is the largest fullerene for which non-IPR isomers of hexaanion and $M_3N@C_n$ will be more stable than IPR isomers. Endofullerenes of this kind, $M_3N@^{s51,365}C_{84}$ (Fig. 4f) (M = Gd, Tb, Tm), have recently been isolated and X-ray crystallographically identified by Dorn, Balch, Echegoyen and colleagues^{66,67} Although other parts

of the structures showed disorder, the metal atom in the fold of the fused pentagons is in full occupancy. The lengths of N–M (M = Gd, Tb, Tm) involving the fused pentagons are also longer than for other N–M bonds, showing the significant coordination of the metal atom to the fused pentagon pair^{66,67}.

To summarize, ${}^{*4,348}C_{66}$ (ref. 19), ${}^{*6,140}C_{68}$ (refs 20,53), ${}^{*6,073}C_{68}$ (ref. 25), ${}^{*7,854}C_{70}$ (ref. 32), ${}^{*10,612}C_{72}$ (ref. 58), ${}^{*10,611}C_{72}$ (refs 59,61,62), ${}^{*17,490}C_{76}$ (ref. 33), ${}^{*22,010}C_{78}$ (ref. 37,64), ${}^{*39,663}C_{82}$ (ref. 65), and ${}^{*51365}C_{84}$ (refs 66,67) have been stabilized by various endoclusters, including metal (scandium or lanthanum) atoms or dimers, nitrides or carbides. However, most of them call for further characterization by X-ray crystallography. The material availability of these unprecedented non-IPR endofullerenes may stimulate the exploration of the special properties that derive from their fused pentagons, their encapsulated metal clusters, or combinations thereof.

Non-IPR fullerenes stabilized by exohedral derivatization

Based on the considerable progress in research of various chemical reactions involving I_h - C_{60} , fullerene chemistry is now a mature discipline⁶⁸. Non-IPR fullerenes can be more reactive than the IPRsatisfying analogues because of the existence of fused pentagons. Therefore, non-IPR fullerenes can be derivatized readily and, in turn, stabilized as exohedral derivatives. As early as 1993, gas-phase experiments⁶⁹ had shown that smaller non-IPR fullerene ions C_n^{*+} could be reduced by butane to form hydrogenated adducts. This suggested that non-IPR fullerenes might be stabilized as exohedral derivatives such as hydrides⁷⁰. However, experiments to stabilize labile non-IPR fullerenes from carbon arc plasma was not reported until 2004 when a smaller fullerene, $^{*271}C_{50}$, was captured by chlorination⁷¹. The structure of $^{*271}C_{50}$ chloride has recently been identified by X-ray crystallography⁷².

Principles for exohedral stabilization of non-IPR fullerenes. Fullerenes are spherical clusters with all their carbon atoms sp² hybridized. Because sp² carbon preferentially adopts planar trigonal symmetry, the curved nature of fullerenes (unlike graphite) causes inherent local strain. The degree of strain is reflected in terms of the POAV pyramidalization angle (θ_p ; ref. 54) at the relevant carbon atom. θ_n for an sp^2 -hybridized carbon is defined as ($\theta\sigma\pi$ -90.0°), where $\theta \sigma \pi$ is the angle between the π -orbital and its three adjacent C–C bonds. Whereas the $\theta_{\rm p}$ value is zero in graphite, for the $I_{\rm h}$ -C₆₀ it is approximately 11.64°. For non-IPR fullerenes, the $\theta_{\rm p}$ values of the carbon atoms along the edges of fused pentagons could be up to about 16°, that is, the $\theta \sigma \pi = 106^\circ$. This value is very close to the regular tetrahedral angle (109.48°) between adjacent sp³-hybridized orbitals of the carbon atom in CH4. So it is reasonable to consider that the carbon atoms in fullerenes, especially those at the pentagon fusions of non-IPR fullerenes, have partial *sp*³ character^{8,9}. Therefore, it will be easier for the fused pentagon carbon atoms of non-IPR fullerenes to bond to another atom or group to form an exohedral derivative. In turn, structural strain relief is achieved through the hybridization of the carbons involved changing from sp^2 to sp^3 . This 'strain-relief principle' has been well supported by available structural geometries of non-IPR fullerene derivatives.

An alternative explanation of such passivation of pentagon fusion comes from the Hückel rule⁹. The two abutted pentagons form an 8π -electron ring, which results in resonance destabilization in terms of Hückel's 4n+2 rule. The fused pentagon bonds are highly antiaromatic with very large negative bond resonance energy⁷³, so various chemical reactions may occur to reduce the number of fused pentagon bonds and stabilize non-IPR fullerenes⁷⁴.

Available structural data on exohedral derivatives of IPR and non-IPR fullerenes have established that stabilities of such derivatives depend heavily on the aromaticity of underivatized sp^2 -hybridized carbon skeletons. In the structure of $^{\#1,809}C_{60}Cl_8$ (ref. 75; Fig. 6), for example, in addition to the four chlorine atoms bonded to the



Figure 6 | Structures of exohedral derivatives. **a**, $C_{20}H_{20}$. **b**, $^{#271}C_{50}CI_{10}$. **c**, $^{#913}C_{56}CI_{10}$. **d**, $^{#1,809}C_{60}CI_{8}$. **e**, $^{#1,804}C_{60}CI_{12}$. **f**, $^{#1,911}C_{64}X_4$ (X=H or CI). **g**, $^{#4,169}C_{66}CI_6$. **h**, $^{#4,169}C_{66}CI_{10}$. The bonds at fused pentagons are red. Parts **a**, **b**, **c** and **f** reprinted from, respectively, ref. 87, © 1982 ACS; ref. 71, © 2004 ACS; ref. 97, © 2008 ACS; ref. 72, © 2008 Wiley. Parts **d** and **e** reprinted from ref. 75, © 2008 NPG.

carbon atoms of the pentagon fusions, a further four chlorines bond to the four carbon atoms at pentagon-pentagon-hexagon vertices to maintain the local aromaticity of the underivatized *sp*²-hybridized carbon skeletons (that is, the aromatic fragments of C₁₀ and C₄₂). The significance of the 'aromaticity' in contributing to the overall stability of fullerene derivatives has also been elaborated by Taylor^{76,77}, Jansen^{78,79} and colleagues in their work on various IPR-satisfying fullerene derivatives including hydrides, hydroxides, halides, oxides, alkyl and aryl-fullerenes, and cycloadducts. Such an 'aromaticity' of *sp*²-hybridized carbon skeletons remaining after exoderivatization, featured with alternation of C-C/C=C single/double bonds, is very similar to the local aromaticity in bowl-shaped polycyclic aromatic hydrocarbons or curved surfaces of fullerenes^{80,81}. We refer to this as the 'local-aromaticity principle', which contributes to the overall stability of the exohedral fullerene molecule and serves to rationalize the observed site-specific exoderivatization of the fullerene cage.

Based on the 'strain-relief' and 'local-aromaticity' principles, many possible structures of non-IPR fullerene exoderivatives can be predicted. As early as 1993, Kroto and co-workers had predicted the existence of some hydrides of small fullerenes (C_n , n = 20, 24, 28, 32, 36 and 50)⁷⁰, among them the D_{5h} -^{#271} C_{50} has now been stabilized as ^{#271} C_{50} Cl₁₀. Many computational studies have recently been conducted for predicting possible structures and electronic properties of non-IPR fullerene exoderivatives, especially for those between C_{60} and C_{70} (or smaller) that inevitably violate the IPR according to Euler's rule. Most of such predicted non-IPR exofullerenes arise from bare fullerene cores that have lower energy and larger HOMO–LUMO gaps among their isomers. Lu and Chen¹³ have recently reviewed the structures, aromaticity, and related chemistry of non-IRP fullerenes with fewer than 60 carbon atoms.

Strategies for synthesis, isolation and identification of non-IPR exofullerenes. Kräschmer–Huffman arc-discharge³⁶ is still the main synthetic approach to exofullerenes. As a result of feeding reactive

Table 3	The fused-pentagon	fullerenes stabilize	d via exohedral	derivatization.
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			Strain-relief rule (angles (°) at the fused pentagons) $\!\!\!\!\!\!^\star$		Local-aromaticity rule	
	Symmetry	Fused pentagons	Fullerene cages [†]	Exohedral derivatives [‡]	(<i>sp</i> ² carbon with aromaticity)	Ref.
C ₂₀ H ₂₀	I _h	1 duodenary directly fused	19.2 to 22.0	1.4	none	13, 87, 88
${}^{\#271}C_{50}CI_{10}$	D_{5h}	5 double fused	15.6	4.4	2 C ₂₀	71, 72
${}^{\#913}C_{56}CI_{10}$	C _{2v}	4 double fused	14.6, 16.3	3.7, 4.4	$C_{\rm 16}andC_{\rm 30}$	97
C ₅₈ F ₁₈	C _s	2 double fused	Not available	Not available	C_4 and C_{36}	83
${}^{\#1,809}C_{60}CI_{8}$	C _{2v}	2 double fused	15.2	3.6	$C_{\rm 10}andC_{\rm 42}$	75
${}^{\#1,804}C_{60}CI_{12}$	<i>C</i> ₁	3 double fused	15.3, 15.2, 15.2	4.0, 4.0, 3.5, 3.4, 2.3, 2.1	$C_{\rm 16}andC_{\rm 32}$	75
$^{\#1,911}C_{64}H_4 \text{ and } \\ ^{\#1,911}C_{64}CI_4$	C _{3v}	1 triple directly fused	16.4, 22.2	4.1, 4.0	C ₆₀	72,100
#4,169C66CI6	<i>C</i> ₁	1 triple sequentially fused	15.8, 16.8	2.9, 2.8, 3.6, 9.7	C_2 and C_{58}	ş
$^{\#4,169}C_{66}CI_{10}$	<i>C</i> ₁	1 triple sequentially fused	15.8, 16.8	2.7, 4.0, 2.3, 9.0	$C_{\scriptscriptstyle 8} and C_{\scriptscriptstyle 48}$	ş

*The angles at the fused pentagons: ¹POAV pyramidalization angle of the carbon atom at the pentagon fusion of a non-IPR fullerene cage; ²Quasi-POAV angles of the relevant sp²-carbon atom at the pentagon fusion, defined by subtracting the regular tetrahedral angle (109.48°) from the average bond angle between the involved C-X (X = substituent group) bond and the three adjoining C-C bonds of a non-IPR fullerene derivative. ⁵Y. Z. Tan *et al.* unpublished work.

agents such as CCl_4 , Cl_2 or CH_4 into the carbon arc plasma during the clustering process, labile non-IPR fullerenes are produced and some of them can be stabilized by chlorine (or hydrogen) radicals *in situ*. Normally, the products from the carbon arc are complex mixtures and the non-IPR fullerene derivatives are synthesized in a relatively low yield. Therefore, separation and purification are necessary to obtain pure materials. The same HPLC techniques used for endofullerene isolation are also applicable to exofullerenes.

Traditional chemical methods have been used for the synthesis of dodecahedrane⁸² ($C_{20}H_{20}$). By the chemical modification of I_h - C_{60} , the fullerene family has been expanded to include carbon cages incorporating four- and seven-membered rings^{83–85}.

All the classical characterization methods, including mass spectrometry, Fourier tranform infrared spectroscopy, NMR spectroscopy and X-ray crystallography, have been applied to the identification of non-IPR exofullerenes. ¹³C NMR spectroscopy is more important than ¹H NMR for structure determination as fullerene derivatives are carbon-rich molecules. The solubility of non-IPR exofullerenes in common organic solvents is often not high enough for acquiring good-quality ¹³C NMR data. Moreover, owing to numerous amounts of structural isomers and poor symmetry of exohedral fullerenes, the ¹³C NMR spectra are usually very complex and authentic structures are hard to assign even in combination with computational studies. At present, X-ray crystallography has become the most important method for characterizing non-IPR exofullerene derivatives with high accuracy, though single-crystal growth is usually a serendipitous event.

Non-IPR fullerenes already stabilized by exohedral methods. In 2000, the species $C_{20}H_mBr_{14-m}$ (m = 1, 2, 3) derivatized from $C_{20}H_{20}$ were debrominated/dehydrogenated into an all-carbon C₂₀ molecule in the gas phase, thereby delivering the smallest fullerene constructed of 12 pentagons⁸⁶. Its dodecahedrane (C₂₀H₂₀) precursor^{87,88}, synthesized in 1982, was the first exohedrally stabilized fullerene derivative, although C₂₀ could not be obtained by cluster growth in carbon plasma. The small fullerene C₃₆ had been claimed to be isolatable, but it coalesces into oligomers and has been derivatized in the form of structurally undefined C₃₆H₆ or C₃₆H₆O derivatives⁸⁹⁻⁹¹. Such coalescence behaviour is also shown by other small fullerenes⁹². In 2004, the non-IPR fullerene ^{#271}C₅₀ was identified, this time stabilized by conventional chlorination in a graphite arcdischarge71. Using similar chlorination or hydrogenation methods, five more non-IPR fullerenes have now been stabilized and identified. Non-IPR fullerene derivatives have also been synthesized starting from IPR-satisfying C₆₀ by chemical modification^{83–85}.

The non-IPR exohedral fullerenes identified so far are shown in Table 3. The derivatization pattern agrees well with the two principles, 'strain-relief' and 'local-aromaticity', proposed for the stabilization of non-IPR fullerenes, even incorporating heptagons or tetragons.

 C_{20} . Dodecahedrane ($C_{20}H_{20}$; Fig. 6a) and its derivatives are special in the non-IPR exofullerene family⁸⁶. It was first synthesized by Paquette and colleagues in 1982^{87,88}, three years before the discovery of the famous I_h - C_{60} . Prinzbach and colleagues^{93,94} developed an efficient 'isodrin–pagodane–dodecahedrane' synthetic route to dodecahedrane. The carbon skeleton of dodecahedrane is an icosahedron containing 12 pentagons, known as the smallest exohedral fullerene⁸⁶. The species C_{20} itself has been generated by electron impact from $C_{20}H_mBr_{14-m}$ (m = 1, 2, 3), but it can only exist in the gas phase with a microsecond lifetime⁸⁶. An unsaturated $C_{20}Cl_{16}$ has been produced by a 'brute-force' photochlorination method⁹⁵. This unsaturated C_{20} derivative, in spite of its extremely bent C=C bonds, proved resistant to oxygen and dimerization (polymerization) but added CH_2N_2 smoothly⁹⁵.

 C_{36} . Zettl's group⁸⁹ reported the preparation and isolation of solid C_{36} , which they identified as a fullerene structure of D_{6d} symmetry. This species was synthesized by graphite arc discharge and separated by sublimation or pyridine-extraction. Time-of-flight mass spectrometry (TOF-MS) showed a dominant peak at 438 amu, 6 amu more than the calculated molecular weight of C₃₆, and assigned as hydrogenated C₃₆. Solid-state ¹³C NMR spectroscopy showed two prominent peaks at 146.1 and 137.5 ppm with a 2:1 relative intensity ratio. On the basis of the NMR and TOF-MS data, the isolated solid was assigned as molecular C_{36} fullerene with D_{6h} symmetry. However, the electron-diffraction pattern of the C36-based solid suggested an intermolecular distance shorter than 1.7 Å, implying the presence of covalent intermolecular bonding. Subsequent theoretical and experimental investigations demonstrated that molecular C₃₆ should be unstable and subject to coalescence as oligomers or derivatization in the forms of C36H4, C36H6 or C36H6O derivatives $^{18,89-91}$. Full structural characterization for these C $_{36}$ derivatives is not yet available.

 C_{50} . C_{50} is the smallest fullerene for which a cage can be constructed without triplets of directly or sequentially fused pentagons^{5,96}. According to the Hirsch spherical aromaticity $2(N + 1)^2$ rule⁸¹, C_{50} has a completely filled electron shell and is highly aromatic. However, the bare C_{50} cage is still too reactive to be isolated in its native form. ${}^{#271}C_{50}$ was captured by chlorine in a graphite arc-discharge process as ${}^{#271}C_{50}Cl_{10}$ (ref. 71). The ${}^{13}C$ NMR spectrum of C_6D_6 shows the high symmetry of this molecule with four signals located at 161.5, 146.6, 143.0 and 88.7 ppm. The first three signals

are characteristic of sp^2 -hybridized carbons and the latter one is typical of an sp^3 -hybridized carbon bonded to chlorine. This Saturn-like D_{5h} -symmetric structure, having two aromatic C_{20} cap moieties connected by five pairs of fused pentagons, has recently been confirmed by X-ray crystallography⁷² (Fig. 6b).

 C_{56} . The strategy of introducing CCl₄ into the carbon arc plasma was also applied to capture the small fullerene, ^{#913}C₅₆ (ref. 97). The stabilized molecule was identified by X-ray diffraction as C_{2v} symmetric ^{#913}C₅₆Cl₁₀ (Fig. 6c). The POAV pyramidalization angles of the two sets of carbon atoms at the adjacent pentagons of the pristine ^{#913}C₅₆ cage are 14.63 and 16.32°, respectively⁹⁸ (Table 3). However, enhanced curvature strain is released as the result of chlorination when the carbons at the pentagon fusions become sp^3 hybridized. The ^{#913}C₅₆Cl₁₀ molecules in the crystal are aligned as entirely straight chains with short Cl…Cl intermolecular distance (3.152 Å) and linear contact of [Cl-C₅₆(Cl₈)-Cl…Cl-C₅₆(Cl₈)-cl…]_n, that may potentially be converted into a useful class of one-dimensional fullerene polymer.

 C_{58} . By fluorination of I_h - C_{60} , two carbon atoms at a hexagonpentagon fusion of I_h - C_{60} were lost to form the stable C_{58} fullerene derivatives, $C_{58}F_{18}$ and $C_{58}F_{17}CF_3$ (ref. 83). The reaction was conducted by Taylor and colleagues *in vacuo* at 550 °C from I_h - C_{60} and lead oxyfluorides containing caesium ($Cs_xPbO_yF_z$). The C_{58} structure for these two derivatives was characterized by mass spectrometry and ¹⁹F-NMR spectroscopy, and has one heptagon surrounded by two pairs of fused pentagons and three hexagons. Figure 7a shows the Schlegel diagram for $C_{58}F_{18}$.

 C_{60} . Two non-IPR C_{60} isomers with C_{2v} and C_s symmetry have recently been stabilized and crystallographically characterized as *^{1,809} $C_{60}Cl_8$ and *^{1,804} $C_{60}Cl_{12}$ (Figs 6d,e)⁷⁵. It has long been suspected that non-IPR C_{60} isomers may be formed during fullerene formation in the gas phase but that they quickly isomerize along the Stone–Wales transformation scheme to form I_h - C_{60} (ref. 99). The capture and identification of the derivatives of these C_{60} isomers has provided experimental evidence in support of the Stone–Wales rearrangement mechanism for fullerene formation, though further experiments are necessary to directly confirm the transformation towards I_h - C_{60} .

C₆₂. The first fullerene with a tetragon, C₆₂, was synthesized by Rubin and colleagues^{84,85} using classical synthesis from I_h -C₆₀. Exohedral derivatives C₆₂X₂ (X = H, 4-MeC₆H₄, 2-Py, 3,5-(MeO)₂C₆H₃) were obtained by formal insertion of a C₂-unit into two adjacent pentagon–hexagon-ring junctions of I_h -C₆₀ (Fig. 7b). The X-ray structure of C₆₂(4-MeC₆H₄)₂ shows that two functional groups are linked at two vertices of the quadrangle, changing the hybridization from *sp*² to *sp*³. Therefore, the strain in the four-membered ring of C₆₂ is released by elongating C–C bonds and enlarging the pyramidalization angle at two carbons of the four-membered ring. The structural feature of I_h -C₆₀ with alternation of C–C/C=C single/double bonds is maintained in C₆₂ derivatives. As seen in Fig. 7b, this non-classical fullerene has no fused pentagon.

C₆₄. The C_{3v}-symmetric fullerene ^{#1,911}C₆₄ with triple directly fused pentagons has been stabilized as ^{#1,911}C₆₄H₄ (ref. 100) and ^{#1,911}C₆₄Cl₄ (ref. 72; Fig. 6f) using the Krätschmer–Huffman method in the presence of CH₄ and CCl₄, respectively. The structure of ^{#1,911}C₆₄H₄ was initially characterized by Wang, Lu and Dunsch using mass spectrometry, ¹³C NMR, FTIR and UV–Vis absorption spectroscopy, linked to *ab initio* calculations¹⁰⁰. It revealed that four hydrogen atoms are added to the carbons at vertices of fused pentagons¹⁰¹. Recently, detailed structural geometry of ^{#1,911}C₆₄Cl₄ has been identified by X-ray crystallography⁷². In the unit cell of ^{#1,911}C₆₄Cl₄, the underivatized *sp*²-hybridized portions are close to each other, and intermolecular interactions are dominated by π - π stacking. There are 16 C···C intermolecular distances shorter than 3.27 Å around the surfaces of each ^{#1,911}C₆₄Cl₄ cage. The four shortest are 3.107 Å, which is about 0.24 Å less than the standard π - π

stacking separation (3.35 Å) seen in layered graphite or multiwall carbon nanotubes. Such strong C···C interactions have potential implications for applications in molecular electronics because of the easier electron transfer between neighbouring fullerene cages in the crystal.

 C_{66} . Although theoretical computations predict that many non-IPR fullerenes could have low-energy isomers with triple sequentially fused pentagons⁵¹, only recently have two non-IPR exofullerenes with such pentagons been stabilized and characterized as ^{#4,169}C₆₆Cl₆ and ^{#4,169}C₆₆Cl₁₀, respectively (Y. Z. Tan *et al.* unpublished work; Figs 6g,h). The two species identified by X-ray crystallography share the same C_s -symmetric parental ^{#4,169}C₆₆ cage with four carbon atoms located at the junctions of the triple sequentially fused pentagons. Of the four carbon atoms in either ^{#4,169}C₆₆Cl₆ or ^{#4,169}C₆₆Cl₁₀, three are chlorinated to give *sp*³-hybridization, whereas the fourth remains unpassivated. That asymmetric chlorination pattern breaks the overall C_s symmetry of parental ^{#4,169}C₆₆ cage, making both ^{#4,169}C₆₆Cl₆ and ^{#4,169}C₆₆Cl₁₀ chiral.

In summary, a total of eight fused-pentagon fullerene cages have been stabilized by exohedral derivatization and fully identified. They are C_{20} , $^{\#271}C_{50}$, $^{\#913}C_{56}$, C_{58} , $^{\#1,809}C_{60}$, $^{\#1,804}C_{60}$, $^{\#1,911}C_{64}$ and $^{\#4,169}C_{66}$. Experimental opportunities now exist for academic and industrial scientists to explore the properties and reactivity of these IPR-defying exohedral fullerenes.

Reactivity of non-IPR fullerenes and their derivatives

Initial gas-phase experiments have demonstrated the high reactivity of non-IPR fullerenes^{1,69,70}. Exohedral chlorination is a useful method for reducing the reactivity of non-IPR fullerenes, but its detailed kinetic and thermodynamic mechanism remains unclear. Recently, two newly isolated non-IPR fullerene chlorides, #4,169C66Cl6 and #4,169C66Cl10 (Y. Z. Tan et al. unpublished work), have been identified. They share the same pristine cage and are formed in the same reaction conditions. This affords a valuable opportunity to investigate the details of the reaction mechanism for chlorination of non-IPR fullerenes. To identify the unprecedented pathways for the formation of ${}^{\#4,169}C_{66}Cl_6$ and ${}^{\#4,169}C_{66}C\bar{l}_{10}$ from parent ${}^{\#4,169}C_{66}$, DFT computations have been performed to optimize the stable structures of ${}^{\#4,169}C_{66}Cl_x$ (x = 1–10) starting from the parent ${}^{\#4,169}C_{66}$ cage. It has been proposed that all the intermediates are the most stable isomers for the given species. They also correspond to the isomers formed by the addition of chlorine to the most active sites of their precursors in each step. Interestingly, computations identified that the existence of the isoenergetic intermediates of #4,169C₆₆Cl₄ give rise to branched reaction pathways that account for the formation of the different chlorides of #4,169C66 under the same experimental conditions. The proposed growth pathways are instructive for constructing unknown non-IPR fullerene derivatives.

Starting from exohedral derivatives of non-IPR fullerenes themselves, the additional groups used to stabilize active pentagon fused



Figure 7 | **Schlegel diagrams of C**₅₈ and C₆₂ **derivatives. a**, C₅₈F₁₈. Fluorine atoms are indicated as blue dots. **b**, C₆₂X₂ (X = H, 4-MeC₆H₄, 2-Py, or 3,5-(MeO)₂C₆H₃); X is represented as blue dots. The heptagon of C₅₈ and the tetragon of C₆₂ are in red. Part **a** reprinted from ref. 83, © 2005 AAAS.

sites could be further substituted by other functionalities to generate multifunctional materials through various chemical reactions such as nucleophilic substitution or Friedel–Crafts reactions. The case of dodecahedrane ($C_{20}H_{20}$) exemplifies how a non-IPR exofullerene can be a useful building block for constructing various multifunctional fullerene-based materials^{82,95}.

For the other IPR-violating fullerenes, because of the difference between fused pentagon sites and other vertices involving hexagons on the surface of non-IPR fullerenes, functional groups at these different sites have often shown different chemical reactivity leading to regiospecific reactions. Friedel-Crafts reactions of #1,809C60Cl8 have exemplified reactivity differences between IPR-satisfying and IPR-violating fullerenes75. A tetra-substituted derivative, $^{\#1,809}C_{60}Cl_4(C_6H_5)_4$, was synthesized in high yield from the reaction of #1,809C60Cl₈ with benzene catalysed by FeCl₃. Longer reaction time did not yield any more-highly substituted species. The structure of ^{#1,809}C₆₀Cl₄(C₆H₅)₄ shows that only four chlorines at the hexagonhexagon vertices are replaced by phenyl groups, whereas the four Cl atoms at the fused pentagon sites remain intact. In comparison, the reaction of ${}^{\#1,812}C_{60}Cl_6$, a typical chlorination derivative of I_h - ${}^{\#1,812}C_{60}$, under the same conditions leads to complete replacement of all six chlorines unless sterically encumbering substituents are used⁶⁸. Theoretical computation has established that the site-specific substitution is due to the higher curvature of fused pentagons in non-IPR ^{#1,809}C₆₀Cl₈. Moreover, ^{#1,809}C₆₀Cl₈ reacting with a mild nucleophile such as methyl glycinate also gives a tetra-substituted derivative, for which structural identification is underway. For the other non-IPR exofullerenes, similar regioselectivites can also be expected.

The reactivity of non-IPR exofullerenes is also shown in $^{#271}C_{50}Cl_{10}$. Preliminary experiments revealed that the chlorines in $^{#271}C_{50}Cl_{10}$ can be replaced by methoxy groups to form a series of $^{#271}C_{50}$ derivatives⁷¹, $^{#271}C_{50}Cl_{10-n}(OCH_3)_n$ (n = 1-4).

Unlike the exohedrally derivatized non-IPR fullerenes, non-IPR endofullerenes still have formally unsaturated sp^2 carbons at the fused-pentagon bond junctions. Thus it is of special interest to elucidate the properties and chemical reactivity of such fused pentagons. Available structural geometries of non-IPR endofullerenes have demonstrated a common rule: the metal atoms of encapsulated clusters are always situated within the region of adjacent pentagon folds. The orientation of the encapsulated metal atoms to the fused pentagons. However, for IPR-satisfying endofullerenes, the interior clusters are usually disordered because of the absence of interactionbonding between the endocluster atoms and the carbon cage.

The encapsulation of endoclusters results in low reactivity of endofullerenes relative to empty fullerenes, and the regioselectivity of endofullerene reactions can be determined by factors such as bond length, pyramidalization and endoclusters¹⁰². As demonstrated for $La@^{\#10,612}C_{72}$ (ref. 58) and $La_2@^{\#10,611}C_{72}$ (refs 61,62), reaction readily takes place at a carbon neighbouring the pentagonpentagon junction. For example, the carbon next to the fused pentagons of $La@^{*10,612}C_{72}$ is subject to reaction both because of the high singly occupied molecular orbital (SOMO) spin-density and the high POAV pyramidalization angle at this position. The two pairs of fused pentagons at each pole of the ${}^{\#10,611}C_{72}$ cage react readily with adamantylidene groups to form bis-carbene adducts of La2@#10,611C72 in high yield⁵⁹. Interestingly, the major bis-adduct isomer shows the two adamantylidene groups covalently bonded to pentagonhexagon junctions (adjacent to the two fused-pentagon bonds) in a symmetric open-cage structure⁶². The resultant structures show that the carbon atoms at the common edge of pentagon-pentagon fusions are not as reactive as those in empty non-IPR fullerenes. The passivation of the fused pentagons by electron transfer from the encaged metal atoms seems to override the expected high reactivity of the carbons of fused-pentagon pairs thought to result from their high surface curvature. Recently Gibson and Dorn¹⁰³ conducted

the Bingel–Hirsch reaction with excess diethyl bromomalonate in the presence of 1,8-diazabicyclo[5.4.0]-undec-7-ene to synthesize a non-IPR endofullerene derivative, the diethyl malonate adduct of Sc₃N@^{#6,140}C₆₈. On investigation using NMR spectroscopy along with DFT computation, they suggested the cyclopropanation of Sc₃N@^{#6,140}C₆₈ also occurred regioselectively at the bond close to the unique fused-pentagon junction.

Future prospects

In the past two decades, fullerene research has been dominated by IPR-satisfying fullerenes (notably I_h - C_{60} and D_{5h} - C_{70}), because they are readily obtained by standard fullerene preparation methods. Although the number of non-IPR fullerenes is vastly larger than IPR-satisfying ones, through topological variety, experimental discoveries of non-IPR fullerenes have only been successful in the past ten years. By endo-encapsulation or exo-derivatization or their combination, more and more non-IPR fullerenes can be expected to be stabilized and identified in the future. The experimental availability of these unprecedented non-IPR fullerenes provides significant materials and creative opportunities for scientists from a wide variety of disciplines to expand their insight into this new world.

Graphite arc-discharge still remains the main route to non-IPR fullerenes, but yields of non-IPR species in mixed products are normally low. Future studies on physical and chemical properties of non-IPR fullerenes will require feasible access to macroscopic quantities. The accessibility of non-IPR fullerenes in such quantities will open up valuable opportunities for experimental investigation of their properties, potentially comparable to the remarkable superconductivity and photophysical properties shown by their cousin $I_{\rm h}$ -C₆₀.

Although only milligram quantities are available at present, the fundamental chemical reactivity of non-IPR fullerenes has already been explored. Unusual structural features and reactivity arising directly from the characteristic fused-pentagons of IPR-violating fullerenes have been observed experimentally and analysed theoretically. Having some advantages over their IPR-satisfying relatives, the fused-pentagon fullerenes are demonstrated to be valuable and versatile building blocks for construction of fullerene-supported supramolecular architectures with potential applications in advanced technologies. Although the chemistry and physics of non-IPR fullerenes are still in their infancy, the scientific curiosity of preparing and understanding these new nanoscale materials and the realistic possibility of finding special properties and practical applications promises them a bright future.

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