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Chlorofullerenes featuring triple sequentially fused pentagons

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The triple sequentially fused pentagons (TSFP) motif is one of the basic subunits that could be used for constructing fullerenes, but it violates the isolated pentagon rule (IPR) and has not been found in carbon cages to date. The properties of TSFP-incorporating fullerenes are thus poorly explored both theoretically and experimentally. Reported herein are four chlorinated derivatives of three different fullerene cages, all with the TSFP motif. X-ray crystallographic analyses indicate that the molecular strain inherent to the pentagon adjacency of a TSFP is significantly relieved upon exohedral chlorination, leaving one of the four pentagon fusion sites unsaturated and rendering the present derivatives chiral. This unique reactivity, in stark contrast to that of previously reported non-IPR fullerenes containing double fused pentagons or triple directly fused pentagons, can be rationalized by density functional theory calculations, and are expected to stimulate further studies of these new members of the fullerene family, both theoretically and experimentally.

Fullerenes are a family of cage-like carbon clusters typically consisting of hexagons and 12 pentagons[1]. Depending on the disposition of the pentagons within the carbon framework, fullerenes can be divided into two distinct types, one characterized by the isolated pentagons and the other by pentagon adjacency. Theoretical and experimental studies have long supported the stability of the first type, generally termed isolated pentagon rule[2] (IPR)-satisfying fullerenes. In contrast, IPR-violating or non-IPR fullerenes are highly reactive, a direct consequence of the high strain and reduced aromaticity originating from the pentagon fusion[3,4]. Because of this, pristine IPR-violating fullerenes have remained elusive, despite extensive efforts having been made. These highly reactive species can nevertheless be stabilized, either by endohedral encapsulation of an electron-donating metal atom/cluster[5–7] or by *sp*^{2}-to-*sp*^{3} rehybridization via exohedral derivatization of the active sites associated with the fused pentagons[8–15]. Note that the latter approach has also been successfully applied to the stabilization of C_{58} (ref. 16) and C_{62} (refs 17,18), which are non-classical fullerenes incorporating a heptagon and a tetragon, respectively.

Two basic configurations of pentagon fusion have been revealed by the structurally characterized derivatives of non-IPR fullerenes, namely double fused pentagons (DFP, Fig. 1a)[5,6,10,13–16] and triple directly fused pentagons (TDFP, Fig. 1b)[11,12]. There exists, however, an alternative configuration when three pentagons are fused; instead of sharing a common carbon vertex as in the case of TDFP, the five-membered rings can be fused sequentially (Fig. 1c). Despite computational predictions[19–23], this triple sequentially fused pentagons (TSFP) motif has never been verified experimentally.

Herein we report four novel fullerene derivatives, $^{\#540}C_{54}Cl_8$ (**1**), $^{\#864}C_{56}Cl_{12}$ (**2**), $^{\#4,169}C_{66}Cl_6$ (**3**) and $^{\#4,169}C_{66}Cl_{10}$ (**4**) obtained by chlorination of the corresponding non-IPR fullerenes $^{\#540}C_{54}$, $^{\#864}C_{56}$ and $^{\#4,169}C_{66}$ (the nomenclature is specified by a spiral algorithm to differentiate isomers[24]). They are the first experimentally established fullerene derivatives featuring TSFP. More importantly, the sharing of this motif suggests its prevalence in the making of various fullerenes, and further research on this particular aspect of fullerene chemistry is expected to shed new light on the mechanism(s) responsible for their gas-phase formation. Furthermore, the unique reactivity towards exohedral derivatization (see below) suggests that many opportunities exist for both theoretical and experimental studies of this unique class of non-IPR fullerenes. Thus, the discovery of TSFP fullerenes portends what promises to be an exciting new direction in fullerene chemistry.

Results

Pure samples of $^{\#540}C_{54}Cl_8$ (**1**), $^{\#864}C_{56}Cl_{12}$ (**2**), $^{\#4,169}C_{66}Cl_6$ (**3**) and $^{\#4,169}C_{66}Cl_{10}$ (**4**) were obtained by multistage recyclic high-performance liquid chromatographic separation from a toluene extract of the fullerene-containing soot (Supplementary Information S1). The purified products are soluble in toluene, chloroform and carbon disulfide, solvents commonly used in fullerene research. The ultraviolet/visible/near-infrared spectra were acquired in toluene solutions (Supplementary Information S2). Single crystals of individual compounds suitable for X-ray diffraction studies were obtained by solvent evaporation of their carbon disulfide or toluene solutions.

The structures of the four compounds have been established crystallographically (Supplementary Information S3) and are shown in Fig. 2. Within the anticipated carbon-cage framework, there exist two sets of TSFP (in **1**), one set of TSFP and two sets

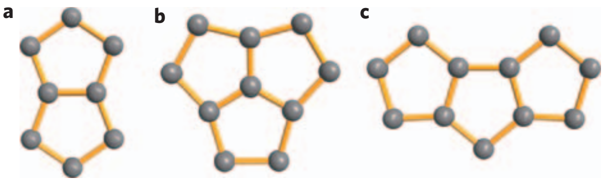

Figure 1 | Basic fused pentagon configurations (with two to three pentagon subunits) in non-IPR fullerenes. a, Double fused pentagons (DFP). **b**, Triple directly fused pentagons (TDFP). **c**, Triple sequentially fused pentagons (TSFP).

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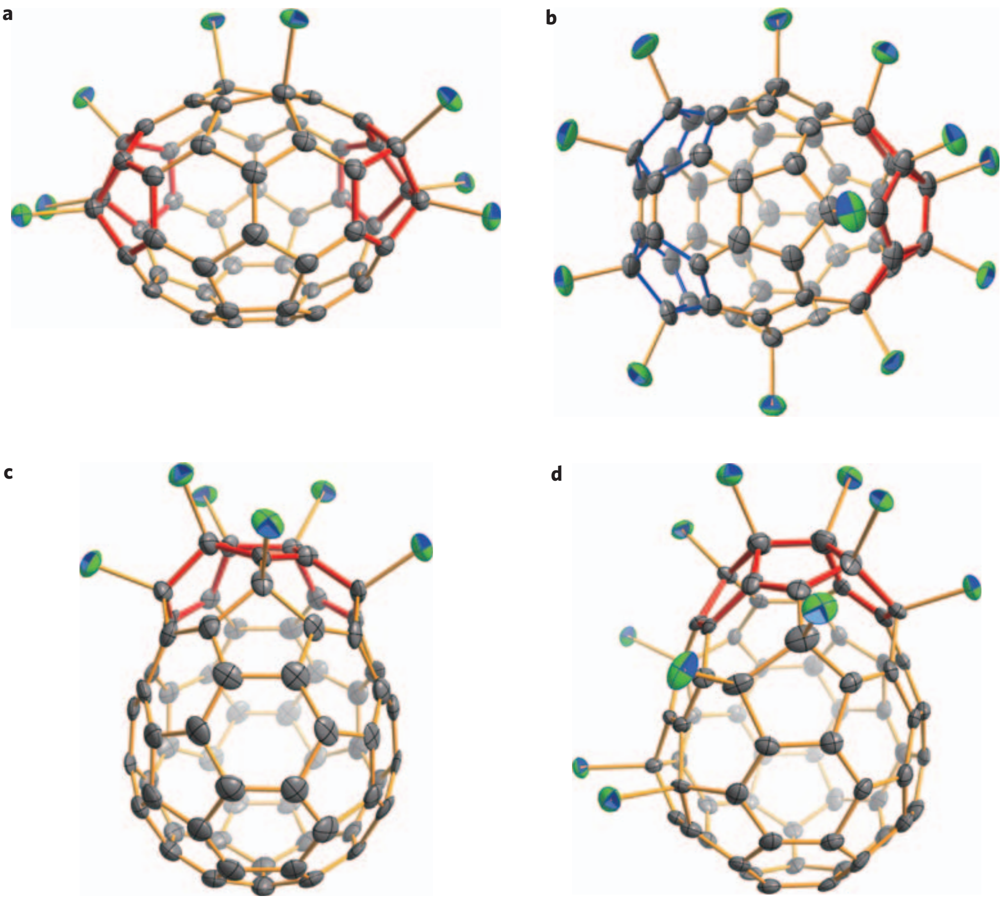

Figure 2 | The structures of $^{\#540}C_{54}Cl_8$ (a), $^{\#864}C_{56}Cl_{12}$ (b), $^{\#4,169}C_{66}Cl_6$ (c), and $^{\#4,169}C_{66}Cl_{10}$ (d). Thermal ellipsoids are shown at 50% probability level. The motifs of TSFP and DFP are highlighted respectively in red and blue. Colour legends of the atoms of interest: Cl, green; C, grey. For clarity, only one enantiomer is shown in each case.

of DFP (in **2**), and one set of TSFP (in both **3** and **4**), in addition to the hexagons and the normal, isolated pentagons. Out of the four carbon atoms (C1–C4) located at the pentagon fusion sites of the TSFP unit, only three of them (C2, C3, C4) are chlorinated to be formally sp^3-hybridized (Figs 2 and 3); the C1 site remains unsaturated in each of these compounds. The key structural parameters including the pyramidalization angles about the carbon atoms at the pentagon fusion sites and the bond lengths associated with the sp^2-hybridized C atoms are summarized in Table 1 and Supplementary Information S7.

Discussion

Four novel chlorinated derivatives, $^{\#540}C_{54}Cl_8$ (**1**), $^{\#864}C_{56}Cl_{12}$ (**2**), $^{\#4,169}C_{66}Cl_6$ (**3**) and $^{\#4,169}C_{66}Cl_{10}$ (**4**) of the corresponding non-IPR fullerenes $^{\#540}C_{54}$, $^{\#864}C_{56}$, and $^{\#4,169}C_{66}$ have been isolated and structurally characterized. As shown in Fig. 2, all compounds display the anticipated basic carbon-cage structure. We note that a species formulated as $C_{54}Cl_8$ has previously been identified by mass spectrometry, but it was not isolated and its structure was unknown at that time[10]. The carbon cage of **2** can be transformed formally from its recently reported cousin of $^{\#913}C_{56}$ (ref. 13) by a single Stone–Wales rotation[25]. As for the fullerene core $^{\#4,169}C_{66}$ shared by **3** and **4**, its structure is intriguingly different from the one that contains two sets of DFP[5].

A common feature shared by these compounds is the presence within the carbon framework of at least one set of TSFP. The existence of abutted pentagons has long been recognized as the primary contributing factor to the instability and high reactivity of non-IPR fullerenes[2]. The stabilization of such species relies therefore on

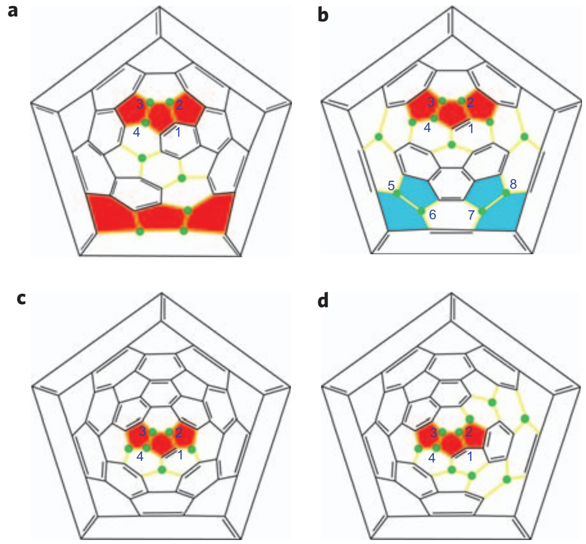

Figure 3 | Schlegel diagrams of $^{\#540}C_{54}Cl_8$ (a), $^{\#864}C_{56}Cl_{12}$ (b), $^{\#4,169}C_{66}Cl_6$ (c), and $^{\#4,169}C_{66}Cl_{10}$ (d). The chlorine atoms are marked as green dots. The TSFP and DFP on the fullerene cages are highlighted as red and blue pentagons, respectively. The carbon atoms at the pentagon fusion sites are numbered. The π-conjugated sp^2 fragments (the C_{46} in $^{\#540}C_{54}Cl_8$, the C_2, C_{14}, and C_{28} in $^{\#864}C_{56}Cl_{12}$, the C_2 and C_{58} in $^{\#4,169}C_{66}Cl_6$, and the C_8 and C_{48} in $^{\#4,169}C_{66}Cl_{10}$) are indicated as alternating C=C/C−C bonds in black.

Table 1 | Key structural parameters of $^{\#540}C_{54}Cl_8$, $^{\#864}C_{56}Cl_{12}$, $^{\#4,169}C_{66}Cl_6$ and $^{\#4,169}C_{66}Cl_{10}$.

Compound	Fused pentagon configuration	Pyramidalization angle θ_p about C atom at the pentagon fusion (°)*			Bond length involving the aromatic or π-conjugated sp^2-C atom	
		Numberation of carbon	Parental cage	Chlorinated derivative	C_n fragment	C–C bond length (Å)
$^{\#540}C_{54}Cl_8$ (**1**)	2 TSFP	C1	16.0	12.0	C_{46}	1.36–1.48
		C2	**16.0**	**2.5**		
		C3	**16.0**	**2.5**		
		C4	**16.0**	**3.9**		
$^{\#913}C_{56}Cl_{12}$ (**2**)	1 TSFP	C1	16.2	9.9	C_2	1.32
		C2	**16.2**	**3.0**	C_{14}	1.37–1.45
		C3	**16.2**	**1.7**	C_{28}	1.35–1.48
		C4	**16.2**	**2.8**		
	2 DFP	**C5**	**15.2**	**3.3**		
		C6	**15.4**	**3.8**		
		C7	**15.4**	**3.8**		
		C8	**15.2**	**4.0**		
$^{\#4,169}C_{66}Cl_6$ (**3**)	1 TSFP	C1	16.8	9.7	C_2	1.32
		C2	**15.8**	**3.5**		
		C3	**15.8**	**2.9**	C_{58}	1.35–1.47
		C4	**16.8**	**2.8**		
$^{\#4,169}C_{66}Cl_{10}$ (**4**)	1 TSFP	C1	16.8	9.0	C_8	1.32–1.42
		C2	**15.8**	**2.7**		
		C3	**15.8**	**2.6**	C_{48}	1.34–1.47
		C4	**16.8**	**3.8**		

*Pyramidalization angle θ_p for an sp^2-hybridized carbon is defined as $(\theta_{\sigma\pi} - 90.0^\circ)$ where $\theta_{\sigma\pi}$ is the angle between the π-orbital and its three adjacent C–C bonds. This concept can be extended to sp^3-hybridized carbons (highlighted in bold) in chlorofullerenes by subtracting 109.47°, the regular tetrahedral angle, from the average angle of the three adjoining Cl–C–C bonds.

means of relieving the molecular strain associated with fused pentagons and achieving local aromaticity of the carbon fragments[4]. The aromaticity is confirmed by the geometrical criteria of the carbon–carbon bond length and is comparable to aromatic molecules already known (see below). We have long been interested in the stabilization and capture of such reactive non-IPR fullerenes through exohedral derivatization of the carbon cage[4], and the present establishment of the four new non-IPR fullerene derivatives further reinforces the validity of this approach.

A scrutiny of the crystal structures reveals significant structural changes and resulting stabilizing effects upon exohedral chlorination. As summarized in Table 1, the pyramidalization angle θ_p—defined as $(\theta_{\sigma\pi} - 90.0^\circ)$ where $\theta_{\sigma\pi}$ is the angle between the π-orbital and its three adjacent C–C bonds and thus a direct indication of the deviation of a fullerene carbon atom from a perfect sp^2-hybridized carbon[26]—is in the range of 15.2–16.8°, comparable to the corresponding values found with other non-IPR fullerenes[4], but significantly larger than the corresponding value of 11.6° in the stable I_h-C_{60} cage (that is, the C_{60} isomer with I_h symmetry). The aggravated curvature contributes to the increase of molecular strain with respect to IPR-satisfying fullerenes and serves as the driving force for exohedral chlorination for strain relief[4]. Indeed, when the concept of the pyramidalization angle is extended to the derivatized sp^3 sites—that is, when the regular tetrahedral angle (109.47°) is subtracted from the average angle of the three adjoining Cl–C–C bonds—a small range of 1.7–4.0° is revealed (Table 1), clearly suggesting the relief of strains inherently associated with the pentagon adjacency. Intriguingly, all but one of the four carbon atoms at the pentagon fusion sites of the TSFP are chlorinated. This is in stark contrast to the other DFP- or TDFP-incorporating non-IPR fullerenes whose pentagon fusion sites are all transformed to be formally sp^3-hybridized through exohedral derivatization. Particularly revealing is the chlorination pattern of **2** whose parental cage contains two sets of DFP and one set of TSFP. The four C atoms at the fusion sites of the DFP sets are all chlorinated, whereas only three of the four TSFP fusion sites are sp^3-hybridized. It appears that the structural adjustment upon chlorination at these sites has already eased the strain at the last pentagon fusion site as the angle θ_p is now sizably smaller than its counterpart in the corresponding parent cage and is comparable to or smaller than that of I_h-C_{60}. Such an asymmetric chlorination pattern breaks the overall symmetries of the parental cages, making all of the present chlorinated derivatives chiral.

Computational studies provide further insights into the chlorination behaviour of the TSFP moiety from a thermodynamic perspective. As an example, density functional theory calculations were performed starting from the bare $^{\#4,169}C_{66}$ cage—the most stable isomer of the 4,478 possible[23]—which is achievable by progressive Cl detachment of **3** or **4** in multistage mass spectrometry (MS^n) (Supplementary Information S4). The gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) predicted at the PBE/DNP level of theory is only 0.95 eV, much smaller than that of I_h-C_{60} (1.67 eV). It has been shown that its HOMO and LUMO coefficients of basis functions are mainly distributed over the TSFP (Supplementary Information S5), and hence the high reactivity is associated with these sites.

In our calculation, each chlorinated species $^{\#4,169}C_{66}Cl_x$ $(x = 1 - 10)$ is the lowest-lying isomer among all isomers possible, and its structure is optimized. It serves as the precursor to the most reactive site(s), which a chlorine atom is added to in the subsequent chlorination step (Supplementary Information S6). As shown in Fig. 4, the formation of **3** and **4** share the first three steps before diverging at the third intermediate $^{\#4,169}C_{66}Cl_3$, in which the spin density is largely distributed over C13 (0.28) and C15 (0.20), but not C1. Further addition of a chlorine atom takes place not surprisingly at C13 or C15, rather than C1, resulting in two isoenergetic isomers $^{\#4,169}C_{66}Cl_4$ (A) and $^{\#4,169}C_{66}Cl_4$ (B), characterized by the asymmetric chlorination pattern with a single unsaturated carbon at the TSFP fusion site (Supplementary Information S6). Intermediates A and B can be viewed as the starting point for the dual chlorination pathway, leading respectively to the formation of **3** and **4**. It should be noted that there exist two isoenergetic isomers for the intermediates $^{\#4,169}C_{66}Cl_5$ and $^{\#4,169}C_{66}Cl_9$ along

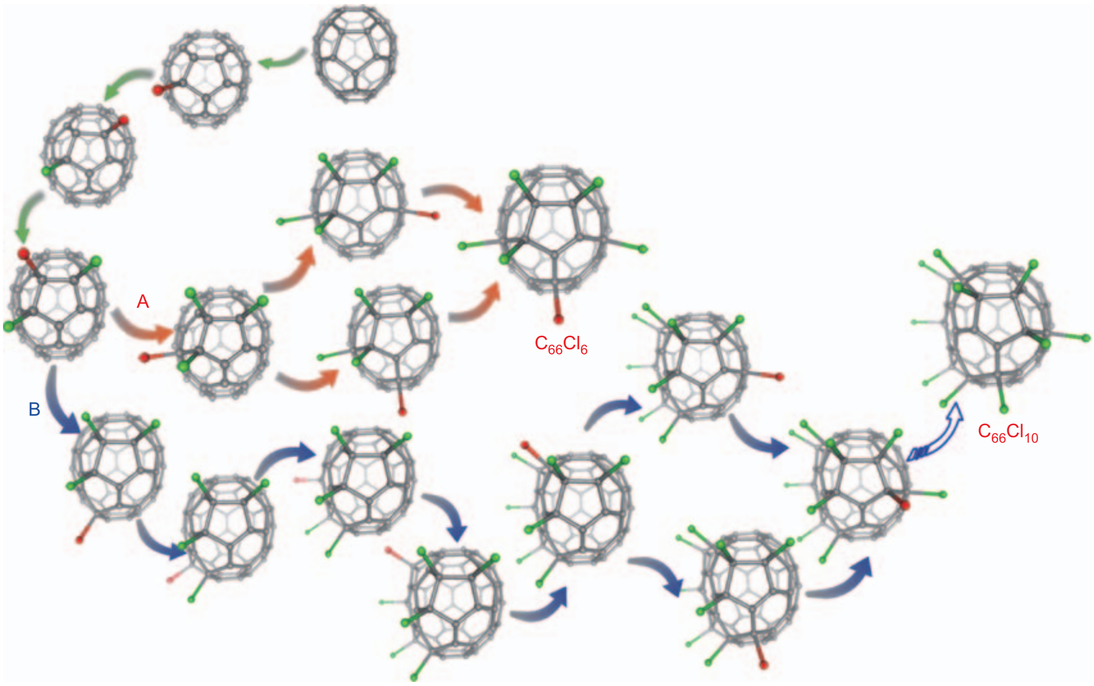

Figure 4 | Chlorination pathways for the formation of $^{\#4,169}C_{66}Cl_6$ and $^{\#4,169}C_{66}Cl_{10}$ from $^{\#4,169}C_{66}$. From the pristine carbon cage $^{\#4,169}C_{66}$, two chlorofullerenes $^{\#4,169}C_{66}Cl_6$ and $^{\#4,169}C_{66}Cl_{10}$ are formed by branched stepwise chlorination processes. This branched chlorination road is led by two isoenergetic $^{\#4,169}C_{66}Cl_4$ intermediates (A and B). The newly added chlorine atom in each intermediate is highlighted in red. The chlorination roads derived from the intermediates A and B are represented by red and blue arrows respectively.

each of these two pathways, but their respective final products, **3** and **4**, remain the same upon further chlorination.

Stabilization via exohedral chlorination is also reflected by the formation of carbon segments displaying either aromaticity or significant π-conjugation[4,27,28]. As summarized in Table 1, these are fragments of C_{46} in **1**, C_2, C_{14} and C_{28} in **2**, C_2 and C_{58} in **3**, and C_8 and C_{48} in **4**. The C_2 pieces in **2** and **3** are ethene-like with a C=C bond length of around 1.32 Å, slightly shorter than the ethene double bond (1.34 Å). Such a short distance for the isolated double bonds may be a typical feature of the chlorinated derivatives of TSFP-incorporating fullerenes. Similarly, the C_8 fragment of **4** is styrene-like with a short isolated double bond (1.32 Å) and a six-electron π-conjugative benzenoid ring with bond lengths ranging from 1.37 to 1.42 Å. The C_{14} moiety of **2** essentially resembles phenanthrene with bond lengths ranging from 1.37 to 1.45 Å. The larger unsaturated pieces of C_{46} in **1**, C_{28} in **2**, C_{58} in **3**, and C_{48} in **4** are bowl-shaped IPR-satisfying fullerene fragments with alternating C=C/C−C bonds, as found in I_h-C_{60}.

In summary, a new class of IPR-violating fullerenes featuring triple sequentially fused pentagons have been captured and isolated as their chlorinated derivatives. Crystallographic studies reveal a unique, incomplete chlorination pattern of the otherwise highly strained and thus reactive TSFP sites. Mechanistic insights have been gained by computational studies regarding the chlorination process, in particular towards the thermodynamics of the stepwise derivatization of these hitherto unknown non-IPR fullerenes. We believe that this work is significant, first and foremost because of its novelty, as this pentagon fusion motif has never been experimentally verified before. The work is also significant because of the prevalence of this newly found structural motif, as suggested by the examples presented herein, which suggests that there are many non-IPR fullerenes yet to be uncovered. Opportunities for theoretical and experimental studies thus abound, and new mechanistic insights into the gas-phase formation of fullerenes and novel TSFP-incorporating fullerene-based materials are to be anticipated.

Methods

The carbonaceous soot containing the chlorinated derivatives of TSFP fullerenes was produced under 0.1974 atm He and 0.0395 atm CCl_4 in a Krätschmer–Huffman arc-discharge reactor[29] equipped with two graphite electrodes, a cathode cylinder block (40 mm (diameter) × 60 mm), and an anode rod (8 mm (diameter) × 300 mm). With a power input of 33 V and 100 A, an hourly production of about 3 g of soot was achieved.

The chlorofullerenes, extracted by toluene in a supersonic bath from the carbonaceous soot, were purified by a multistage high-performance liquid chromotography (HPLC) process using a Cosmosil Buckyprep column (inner diameter 10 × 250 mm), a Buckyprep-M column (inner diameter 10 × 250 mm) and then a Buckyprep column (inner diameter 4.6 × 250 mm), sequentially (Supplementary Information S1). The HPLC chromatograms were obtained on a Shimadzu LC-6AD HPLC instrument. The mass spectra and MS^n spectra were acquired on a Bruker HCT mass instrument. The crystallographic data were collected on a Bruker Smart Apex-2000 CCD diffractometer or an Oxford CCD diffractometer. The ultraviolet/visible/near-infrared spectra were recorded on a Varian Cary 5000 spectrophotometer.

Geometry optimizations of pristine $^{\#540}C_{54}$, $^{\#864}C_{56}$, $^{\#4169}C_{66}$, and the chlorinated derivatives of $^{\#4169}C_{66}$, $^{\#4169}C_{66}Cl_x$ ($x = 1$–10), were performed using the generalized gradient approximation PBE functional of density functional theory[30] with all-electron double numerical basis sets plus polarization (DNP) implemented in the $Dmol^3$ package[31].

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Author contributions

S.Y.X., L.S.Z. and R.B.H. conceived and designed the experiments, S.Y.X., Z.P.Z. and X.L. co-wrote the paper, Y.Z.T. completed the identification, Y.Z.T. and X.H. performed the isolation, F.Z. and Z.J.L. conducted the synthesis, X.L. and J.L. performed the theoretical work, W.S.J., Z.Z.Q. and R.T.C. participated in early isolation experiments. All authors discussed the results and commented on the manuscript.

Additional information

The authors declare no competing financial interests. Supplementary information and chemical compound information accompany this paper at www.nature.com/naturechemistry. Reprints and permission information is available online at http://npg.nature.com/reprintsandpermissions/. Correspondence and requests for materials should be addressed to S.Y.X. and X.L.