

## C<sub>72</sub>Cl<sub>4</sub>: A Pristine Fullerene with Favorable Pentagon-Adjacent Structure

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**Abstract:** A long-sought empty non-IPR fullerene, <sup>#11188</sup>C<sub>72</sub>, which is more stable than the sole IPR isomer in the fullerene[72] family, has been retrieved and crystallographically characterized as <sup>#11188</sup>C<sub>72</sub>Cl<sub>4</sub>. Mass spectrometric data support the facile dechlorination of <sup>#11188</sup>C<sub>72</sub>Cl<sub>4</sub> and, in turn, the possible stability of pristine <sup>#11188</sup>C<sub>72</sub>.

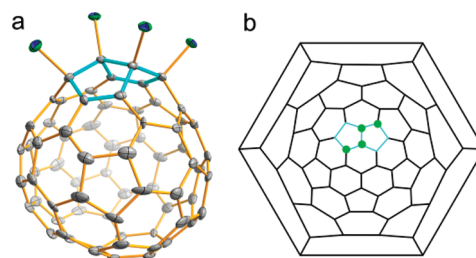
It has been widely accepted that the most stable hollow fullerene among all possible cage-closed structures built from a number of hexagons and 12 pentagons is a structure having each pentagon isolated.<sup>1,2</sup> In other words, the stability of an all-carbon fullerene without any chemical modification, such as exohedral or endohedral derivatization, is governed by the isolated pentagon rule (IPR).<sup>2</sup> Outside the gas phase, all of the experimentally available pure fullerenes synthesized to date devotedly satisfy this rule.<sup>3</sup> Topologically, a cage with all pentagons isolated (i.e., an IPR fullerene) can be built for C<sub>60</sub>, C<sub>70</sub>, and fullerenes larger than C<sub>70</sub>.<sup>4</sup> Among them, the most notable one is *I<sub>h</sub>*-symmetric <sup>#1812</sup>C<sub>60</sub>, which was originally synthesized in macroscopic quantities in the early 1990s (the nomenclature used here employs the Fowler–Manolopoulos spiral algorithm<sup>4</sup> to differentiate the isomers). In the range from C<sub>70</sub> to C<sub>96</sub>, representative empty IPR isomers with any given cluster size have been fully characterized also.<sup>5</sup> The only exception has been seen for C<sub>72</sub>: an empty fullerene with the cluster size of 72 atoms has never been isolated and characterized, even though C<sub>72</sub> has an IPR isomer with *D<sub>6d</sub>* symmetry. A few metallofullerenes of C<sub>72</sub> (e.g., La<sub>2</sub>@<sup>#10611</sup>C<sub>72</sub>, La@<sup>#10612</sup>C<sub>72</sub>, and Ce<sub>2</sub>@<sup>#10611</sup>C<sub>72</sub>) have been stabilized through the electron transition from the encapsulated metal atom(s) to the fullerene cage,<sup>6–10</sup> but these endofullerenes are not obligated to establish the stability of the pristine cages involved. The difficulty in retrieving pristine C<sub>72</sub> may be due to the structural instability of the IPR isomer, i.e., the *D<sub>6d</sub>*-symmetric <sup>#11190</sup>C<sub>72</sub>. Published estimates have revealed that <sup>#11190</sup>C<sub>72</sub> is the sole IPR isomer but the second most stable structure in the pristine C<sub>72</sub> family. Its energy is 11–15 kcal/mol higher than the non-IPR isomer <sup>#11188</sup>C<sub>72</sub>, and its entropy is also unfavorable.<sup>11–14</sup> This exemplifies an unusual case of a hollow fullerene preferring a more favorable non-IPR structure. However, experimental evidence for the existence of such a non-IPR species has not been obtained to date. In this contribution, we report our success in capturing and isolating this molecule as <sup>#11188</sup>C<sub>72</sub>Cl<sub>4</sub> from the products of a graphite arc discharge involving CCl<sub>4</sub>. The avenue for experimental investigation of this unusual fullerene is therefore open.

The <sup>#11188</sup>C<sub>72</sub>Cl<sub>4</sub>-containing soot was produced in a Krätschmer–Huffman carbon arc reactor charged with 0.0395 atm CCl<sub>4</sub> and 0.1974 atm helium.<sup>15,16</sup> The collected soot (~200 g) was supersonically extracted with toluene at room temperature. Upon separation by multistage high-performance liquid chromatography (HPLC), ~10 mg of <sup>#11188</sup>C<sub>72</sub>Cl<sub>4</sub> with high purity was

isolated from the toluene-soluble components of the soot [the detailed separation procedure is described in the Supporting Information (SI)].

By solvent evaporation from a carbon disulfide solution, black-colored single crystals suitable for X-ray diffraction determination were grown. Shown in Figure 1 are the molecular geometry and the Schlegel diagram of <sup>#11188</sup>C<sub>72</sub>Cl<sub>4</sub> identified by X-ray crystallography. The overall molecule looks like a “pineapple” with four covalently attached “leaves”, each consisting of one chlorine atom. It is similar to another pineapple-shaped molecule, C<sub>64</sub>Cl<sub>4</sub>, but has a larger body size.<sup>17</sup>

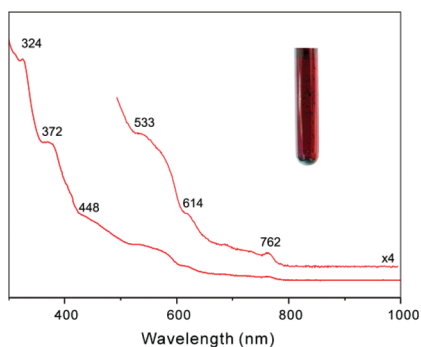
The present <sup>#11188</sup>C<sub>72</sub> molecule was captured in situ by chlorination and directly isolated from the products of the carbon arc discharge, which is a typical venue for bottom-up growth of carbon allotropes. This is different from the non-IPR C<sub>76</sub>Cl<sub>24</sub> and heptagon-incorporating C<sub>84</sub>Cl<sub>32</sub> that were synthesized in off-line experiments through chlorination transformation or top-down detachment of a C<sub>2</sub> unit from a stable fullerene (C<sub>76</sub> or C<sub>86</sub>).<sup>18,19</sup>



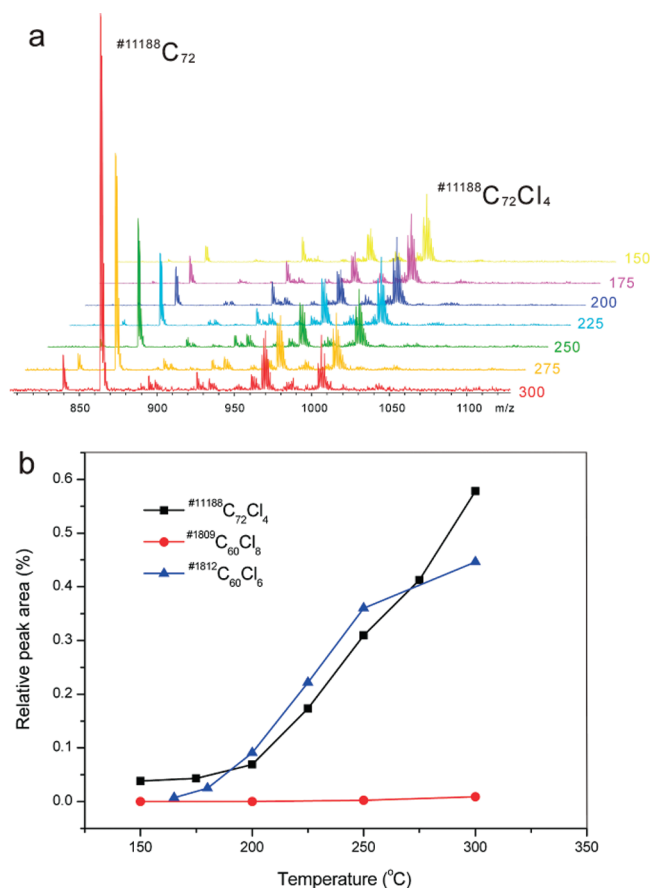
**Figure 1.** Structures of <sup>#11188</sup>C<sub>72</sub>Cl<sub>4</sub>. (a) ORTEP drawing with thermal ellipsoids at the 30% probability level. The fused pentagons in the structure are highlighted in blue. (b) Schlegel diagram of <sup>#11188</sup>C<sub>72</sub>Cl<sub>4</sub> in which the chlorine atoms are indicated by green dots.

The chlorination pattern of the molecule can be rationalized by both the “strain-relief” and the “local-aromaticity” principles.<sup>3</sup> Primarily, the fusion atoms of the adjacent pentagons are respectively bonded with two of the chlorine atoms to release the unfavorable local strain. In addition, two chlorine atoms are bonded at two additional pentagon–hexagon–hexagon vertexes to change the hybridization of the involved carbons from sp<sup>2</sup> to sp<sup>3</sup>. The resultant substructure containing the remaining 68 sp<sup>2</sup>-hybridized carbon atoms is in accord with the “local-aromaticity” principle as defined in ref 3. These two principles are acceptable for exohedral stabilization of other non-IPR fullerenes, such as the recently reported non-IPR C<sub>76</sub>Cl<sub>24</sub>.<sup>18</sup>

Purified <sup>#11188</sup>C<sub>72</sub>Cl<sub>4</sub> has a vivid dark-red color in toluene solution and shows UV–vis–NIR absorption over a wide range of wavelengths (Figure 2). In addition to the longest absorption at 762 nm, a series of strong absorptions are located at 614, 533, 448,



**Figure 2.** UV-vis-NIR spectrum of  $^{1188}\text{C}_{72}\text{Cl}_4$  in toluene. The inset is a photograph of a toluene solution of  $^{1188}\text{C}_{72}\text{Cl}_4$ .



**Figure 3.** Thermal dechlorination of  $^{1188}\text{C}_{72}\text{Cl}_4$ . (a) Mass spectra of  $^{1188}\text{C}_{72}\text{Cl}_4$  obtained at different ionization temperatures. (b) Decomposition curves of  $^{1188}\text{C}_{72}\text{Cl}_4$ ,  $^{1812}\text{C}_{60}\text{Cl}_6$ , and  $^{1809}\text{C}_{60}\text{Cl}_8$ . The data for  $^{1812}\text{C}_{60}\text{Cl}_6$  and  $^{1809}\text{C}_{60}\text{Cl}_8$  were taken from ref 20 for comparison.

372, and 324 nm. Such a wide range of absorption may be useful for technological applications in some fields such as fullerene-based solar cells.

The molecular composition of  $\text{C}_{72}\text{Cl}_4$  was confirmed by mass spectrometry (MS) using an atmospheric pressure chemical ionization (APCI) source. As shown in Figure 3a, the most prominent feature of the mass spectra is the occurrence of the strong peak at  $m/z$  864, corresponding to a 72-atom carbon cluster, in addition to the molecular ions ( $m/z$  1004–1010) with the featured isotopic pattern of  $\text{C}_{72}\text{Cl}_4$ . In agreement with the multistage mass spectra (see the SI), this strong peak can be assigned to the bare  $^{1188}\text{C}_{72}$  cage produced by progressive dechlorination of  $^{1188}\text{C}_{72}\text{Cl}_4$ . To establish the facile dechlorination of  $^{1188}\text{C}_{72}\text{Cl}_4$  and the possible

stability of bare  $^{1188}\text{C}_{72}$ , we performed a series of APCI mass spectrometric experiments with different furnace temperatures under otherwise the same analytical conditions. The detachment of chlorine from the chlorofullerene was quantified by a curve with the relative peak area of the fully dechlorinated bare fullerene versus the furnace temperature (Figure 3b). The relative peak area of the resultant bare fullerene, which is associated with the degree of chlorine detachment from the mother chlorofullerene and the stability of the pristine cage involved, is defined as the MS peak area proportion of the bare fullerene signal in all of the corresponding fragments of the chlorofullerene.<sup>20</sup> It is obvious that at a temperature higher than 250 °C, the pristine  $^{1188}\text{C}_{72}$  cage is produced dominantly. In contrast, however, the dechlorination reaction involving other non-IPR chlorofullerenes such as  $^{1809}\text{C}_{60}\text{Cl}_8$  remains silent at this temperature (Figure 3b).<sup>20</sup> As shown in Figure 3b, the detachment of chlorine from the mother chlorofullerene  $^{1188}\text{C}_{72}\text{Cl}_4$  is even comparable with the dechlorination from  $^{1812}\text{C}_{60}\text{Cl}_6$  having a stable fullerene cage. This evidence supports the facile dechlorination of  $^{1188}\text{C}_{72}\text{Cl}_4$  and, in turn, the possible stability of pristine  $^{1188}\text{C}_{72}$ . This also agrees with the possibility that the bare  $^{1188}\text{C}_{72}$  may grow up in the arc zone at high temperature and subsequently be captured by chlorine atoms that happen to be produced from  $\text{CCl}_4$  under the carbon-arc conditions.

According to the Hirsch spherical aromaticity  $2(N + 1)^2$  rule,<sup>21</sup>  $\text{C}_{72}$  has a completely filled electron shell (with  $N = 5$ ) and is spherically aromatic. However, the  $2(N + 1)^2$  rule alone is not enough to predict the relative stability of different isomers for a given carbon cluster. Theoretical calculations have predicted that non-IPR  $^{1188}\text{C}_{72}$  is the most favorable isomer among other  $\text{C}_{72}$  isomers with respect to both energy and entropy.<sup>11–14</sup> Obviously, this conclusion contradicts the IPR rule.<sup>2</sup> Martin proposed an additional sphericity to account for the stability of a molecule if nearly spherical shapes can be built by increasing the number of adjacent pentagons.<sup>22</sup> The present work provides an experimental clue to validate these theoretical proposals on such an unusual fullerene with a more favorable non-IPR structure.

In conclusion, the first pristine fullerene[72] has been retrieved and identified by X-ray crystallography as  $^{1188}\text{C}_{72}\text{Cl}_4$ . This non-IPR fullerene is outstanding for having a higher stability than its IPR isomer. In agreement with the theoretical prediction, mass spectrometric data support the facile dechlorination of  $^{1188}\text{C}_{72}\text{Cl}_4$  and the possible stability of bare  $^{1188}\text{C}_{72}$ . This work renders the energy-favorable non-IPR fullerene[72] as an experimentally viable member in the family of  $\text{C}_{72}$ , and further theoretical and experimental activities on this unusual cage are highly expected.

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**Supporting Information Available:** Crystallographic data (CIF), HPLC separation procedure, and multistage mass spectra of  $\text{C}_{72}\text{Cl}_4$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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