Gigantic C_{120} Fullertubes: Prediction and Experimental Evidence for Isomerically Purified Metallic [5,5] C_{120}-D_{5d}(1) and Non-Metallic [10,0] C_{120}-D_{5h}(10766).

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ABSTRACT: We report the first experimental characterization of isomerically pure and pristine C_{120} fullertubes, [5,5] C_{120}-D_{5d}(1) and [10,0] C_{120}-D_{5h}(10766). These new molecules represent the highest aspect ratio fullertubes isolated to date, *e.g.*, the prior largest empty cage fullertube was [5,5] C_{100}-D_{5d}(1). This increase of 20 carbon atoms represents a gigantic leap in comparison to *three decades* of C_{60}-C_{90} fullerene research. Moreover, the [10,0] C_{120}-D_{5h}(10766) fullertube has an endcap derived from C_{80}-D_{5h} and is a new fullertube whose C_{40} endcap has not yet been isolated experimentally. Theoretical and experimental analysis of anisotropic polarizability and UV-vis assign C_{120} isomer I as [5,5] C_{120}-D_{5d}(1) fullertube. C_{120} isomer II matches a [10,0] C_{120}-D_{5h}(10766) fullertube. These structural assignments are further supported by Raman data showing metallic character for [5,5] C_{120}-D_{5d}(1) and nonmetallic character for C_{120}-D_{5h}(10766). STM imaging reveals a tubular structure with an aspect ratio consistent with a [5,5] C_{120}-D_{5d}(1) fullertube. With microgram quantities not amenable to crystallography, we demonstrate that DFT anisotropic polarizability, augmented by long-accepted experimental analyses (HPLC retention time, UV-vis, Raman, and STM) can be synergistically used (with DFT) to down select, predict, and assign C_{120} fullertube candidate structures. From 10,774 mathematically possible IPR C_{120} structures, this anisotropic polarizability paradigm is quite favorable to distinguish tubular structures from carbon soot. Identification of isomers I and II was surprisingly facile, *i.e.*, 2 purified isomers for 2 possible structures of widely distinguishing features. These metallic and non-metallic C_{120} fullertube isomers open the door to both fundamental research and application development.

The *experimental* discovery and isolation[1] in 2020 of pristine [5,5] C_{100}-D_{5d}(1) fullertubes is generating enthusiasm based on their unique molecular architecture. With reproducible structures and defined molecular weights, fullertubes possess the trifecta of structural motifs found in fullerenes (endcaps), nanotubes (belt), and rolled graphene (m,n).

Of broad interest is whether fullertubes behave as fullerenes (C_{60}, C_{70}), as single wall nanotubes (SWNTs), or neither. In 2021, a study[2] showed a transition to metallic properties by inserting 10 carbon atoms from the shorter [5,5] C_{90}-D_{5h}(1) fullertube to the longer [5,5] C_{100}-D_{5d}(1) fullertube. In 2022, an excited state study[3] of [5,5] C_{90}-D_{5h}(1) fullertubes showed photophysical properties consistent with classical fullerenes. However, the longer [5,5] C_{100}-D_{5d}(1) fullertube broke the trend[3] expected for fullerene behavior and suggested unique properties for C_{100} fullertubes. A separate study in 2022 evaluated the catalytic behavior of fullertubes.[4] Therein, C_{96}-D_{3d}(3) fullertube was successful as a metal-free O_2-reduction electrocatalyst.[4]

Herein, we report the discovery of *two* new isomerically purified C_{120} fullertubes (Figure 1). Supported by experimental and DFT calculations (Figure 2), isomer II is a C_{80}-based end cap fullertube, [10,0] C_{120}-D_{5h}(10766). This species suggests a new fullertube family (C_{40} + C_{40} + C_{20n}, where n = number of carbon belts). For [10,0] C_{120}-D_{5h}(10766), this work represents the first experimentally purified and characterized [10,0] fullertube.

Experiments include UV-vis, Raman, XPS, and STM imaging. Earlier attempts to purify C_{120} fullerenes[5] or fullertubes[1] failed to permit isomerically pure and pristine samples. Below we show the complete isomeric separation and characterization of both new C_{120} molecules: metallic [5,5] C_{120}-D_{5d}(1) and non-metallic [10,0] C_{120}-D_{5h}(10766) fullertubes.

Putting this C_{120} fullertube experimental isolation into historical context, more than 30 years elapsed since C_{60} and C_{70} were first prepared in macroscopic quantities in the 1990s.[6] Twenty years passed before the [5,5] C_{90}-D_{5h}(1) fullertube was reported in 2010.[7] The halogenated derivative of C_{100} was not reported until 2014.[8] It took another six years (2020) to experimentally isolate [5,5] C_{100}-D_{5d}(1) in *pristine* form, and the larger C_{120} species was obtained as an isomeric mixture.[1] There was no experimental support to distinguish C_{120} as being spherical or tubular in shape.

The C_{120} discovery began with down selecting 10,774 possible[5] IPR (isolated pentagon rule)[9] structural isomers. This initial elimination of C_{120} candidates was facilitated by our recent discovery[1] of a selective reaction that removes from consideration *spheroidal and ellipsoidal* cages based on numerous 5,6 ring junctions *i.e.*, facile reaction with aliphatic amines.[10] In contrast, fullertubes possess a protective tubular belt of 6,6 junctions and are more chemically resistant to amine attack. Because only a very small number of C_{120} structures (of the 10,774 isomers) are tubular, this initial screening dramatically reduces the list to just a few possibilities. Note, the highly symmetrical and tetrahedral C_{120}-T_d (4814) fullerene is predicted[11] to be quite stable. If originally present in soot extract, C_{120}-T_d would have been reacted and removed.

Figure 1 puts this work into context, beyond the shortest fullertube, [5,5] C_{90}-D_{5h}(1),[7] beyond the [5,5] C_{100}-D_{5d}(1),[1] to now include the [5,5] C_{120}–D_{5d}(1) fullertube. This increase of *twenty atoms* from C_{100} to C_{120} represents the largest and longest empty-cage fullertube to be isolated and characterized to date. Moreover, the [5,5] C_{120}-D_{5d}(1) fullertube (isomer I) represents a *third* member (C_{90}, C_{100}, and C_{120}) of a theoretically predicted[12] C_{30} + C_{30} + C_{10n} fullertube family. Note that within this [5,5] family (*i.e.*, C_{60} + C_{10n}, where n = number of tubular belts), there are three predicted series[13] of fullertubes (Figure 1 inset). For context, C_{120}-D_{5d}(1) belongs to the N=30n lineage, *e.g.*, Series 1: C_{60}, C_{90}, C_{120}, C_{150}, and so forth.

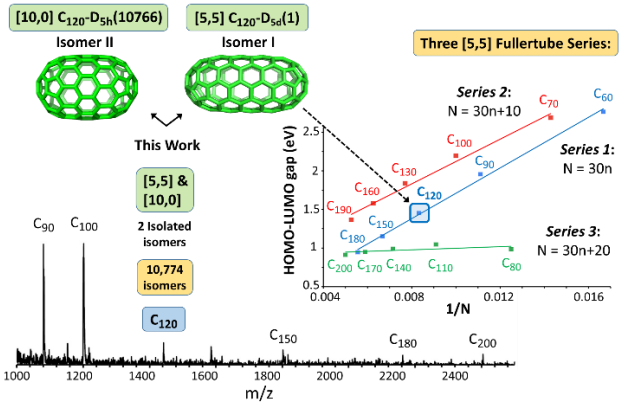


Figure 1. LDI mass spectrum of C_{90}, C_{100}, and C_{120} fullertubes (bottom left) and HOMO-LUMO plot for the three [5,5] fullertube mathematical series (upper right, N = number of carbon atoms).

Our second round of down selection compares DFT and experimental values of anisotropic polarizability obtained from HPLC retention time analysis, Figure 3d (see S7 for anisotropic polarizability details). The correlation of polarizability versus retention time of fullerene cages has been previously reported.[14, 15]

A third down selection compared DFT calculated UV-vis versus experimental spectra (Fig. 2 and 3). A fourth down selection used Raman analysis to distinguish between [5,5] metallic versus nonmetallic [10,0] fullertubes. A fifth layer of experimental support was STM imaging (Figure 5). Geometric analysis (see S9) of the image confirmed a tubular shape and an aspect ratio with dimensions of 0.74 nm (diameter) and 1.53 nm (length).

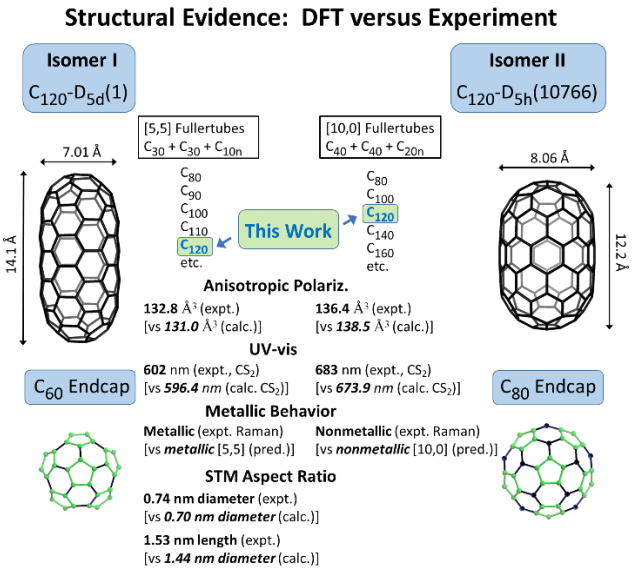


Figure 2. Summary of DFT and experimental evidence for [5,5] C_{120}-D_{5d}(1), Isomer I versus [10,0] C_{120}-D_{5h}(10766), Isomer II.

In hindsight, both C_{120} isomers I and II could have been structurally assigned after only *two* rounds of refinement, *i.e.*, just using chemical selectivity with amines (Round 1) and anisotropic polarizability (Round 2) from retention time data. For C_{120}, Rounds 3 (UV-vis), 4 (Raman), and 5 (STM imaging) were not needed for structural determination, but nevertheless provided additional layers of independent confirmation.

For C_{120}, there were exactly *two* isolated unknowns to match from a pool of only *two* possible candidates, [5,5] C_{120}-D_{5d}(1) and [10,0] C_{120}-D_{5h}(10766). All other IPR structures were a mismatch. For example, Figure 4 shows the nearest candidate of C_{120}-D_{5d}(10765) has a too low anisotropic polarizability value (112.1 Å^3) significantly distant from either isomer I, 131.0 Å^3 (132.8 Å^3, expt.) or isomer II, 138.5 Å^3 (136.4 Å^3, expt.). Further detail on the units of polarizability (Å^3) and its anisotropy (Å^6) are provided by Sabirov.[16] Moreover, C_{120}-D_{5d}(10765) could have also been eliminated based on its mismatched UV-vis profile (573.4 nm, calc.) when compared to isomer I, 596.4 nm (602 nm, expt.) or isomer II, 673.9 nm (683 nm, expt.).

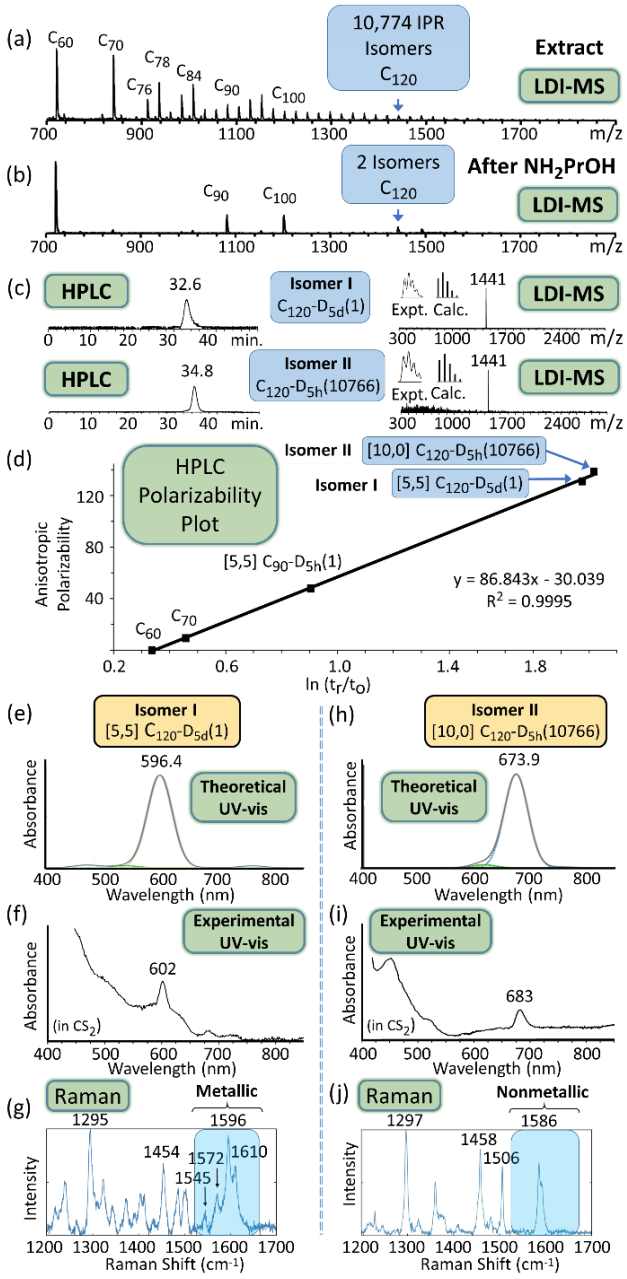


Figure 3. LDI mass spectra of (a) soot extract before amine attack (b) unreacted species remaining in solution, (c) HPLC and LDI mass spectra for purified C_{120} isomers, (d) correlation of anisotropic polarizability to retention time (see S5 for x,y,z coordinates and S7 for polarizability details), (e,h) DFT UV-vis, (f,i) experimental UV-vis spectra, and (g,j) experimental Raman spectra.

The breakthrough[1] for isolating fullertubes arrived in 2020 via a selective reaction, wherein tubular carbon and spheroidal fullerenes are separated. Leveraging differences in amine reactivity, C_{90} and C_{100} fullertube concentrations improved by factors of 100 and 1000.[1] For this C_{120} work, our experimental approach is summarized in Scheme 1. We purified two structural isomers of C_{120} fullertubes from soot extract (Fig. 3a) using three stages of chemical selectivity (see S1).

Stage 1 reacts and removes *spheroidal* fullerenes (C_{76}-C_{200}) as water soluble derivatives. Tubular shaped carbon (fullertubes) remain in the organic layer (Fig. 3b). Total isomeric resolution of C_{120} fullertubes required HPLC selectivity of BuckyPrep-M (Stage 2) and PYE (Stage 3) stationary phases with multiple repeated injections due to their similar retention times, *e.g.*, isomer I, [5,5] C_{120}-D_{5d}(1), at 32.6 and isomer II, [10,0] C_{120}-D_{5h}(10766), at 34.8 minutes, respectively (Fig. 3c). Final purified samples were monitored by *online* HPLC-UV-vis detection. Specifically, multiple UV-vis spectra (from a PDA detector) were taken across the HPLC peak profile (front, mid, and tail region) and showed the absence of spectral peaks from the neighboring isomer (see S11). The isolated yield of each purified C_{120} fullertube isomer was less than 50 micrograms.

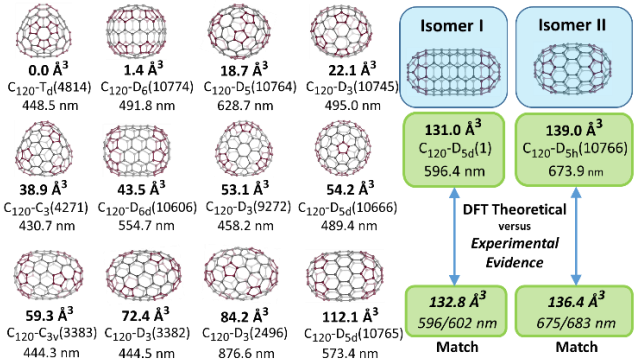
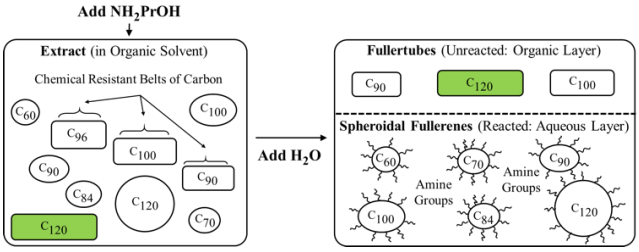


Figure 4. Down selection of high symmetry (3-fold and higher) C_{120} IPR structures (see S10 for criteria on high symmetry isomer selection), anisotropic polarizability, and UV-vis comparison.



Scheme 1. Overview of selective separation to remove spheroidal fullerenes by imparting hydrophilicity. C_{90}, C_{100}, and C_{120} fullertubes remain largely unreactive in aromatic solvent (S1).

We compared experimental versus DFT anisotropic polarizabilities of the candidate isomers (Fig. 4). A [5,5] C_{120}-D_{5d}(1) assignment agrees with anisotropic polarizability values, *e.g.*, 132.8 Å^3 (calc.), 131.0 Å^3 (expt.). Likewise, Isomer II is in excellent agreement with [10,0] C_{120}-D_{5h}(10766), *e.g.*, 138.5 Å^3 (calc.), 136.4 Å^3 (expt.). For context, an important and readily computed DFT parameter for fullerenes is their polarizability and anisotropic polarizability because they are related to the experimental HPLC chromatographic retention time and capacity factor, k' (see S7). Kappes and coworkers[17] have mathematically described the effect of polarizabilities, dipole moments, and ionization potentials. For fullerenes, the polarizability is directly proportional to the experimental chromatographic retention parameter, ln (t_r/t_o). Further work by Sabirov[15] indicates the anisotropic polarizability is an even better parameter for establishing subtle differences in fullerene derivatives. The effect of polarizability on retention time has explained the

HPLC elution behavior of empty-cage fullerenes and metallofullerenes.[14, 15]

There are only 13 IPR allowed C_{120} isomers with 3, 5, and 6 fold symmetry (see S4). To date, fullertubes isolated via this chemical separation protocol, *i.e.*, C_{90}-D_{5h}, C_{96}-D_{3d}, C_{100}-D_{5d}, [5,5] C_{120}-D_{5d}(1) and [10,0] C_{120}-D_{5h}(10766) all have endcaps derived from C_{60}-I_h hemispheres or other high symmetry common hemispheres from metallofullerene chemistry (*e.g.*, C_{80}-D_{5h}) with high symmetry (see S6). Further details on the criteria for selecting the 3, 5, and 6 fold isomers are described in S10. The DFT calculated properties for these 13 isomers are described in Figure 4, S2, and S3.

Our third layer of structural support compared experimental and theoretical UV-vis spectra for each C_{120} isomer (Figure 3). For isomer I, the DFT dominant 596 nm peak (Fig. 3e) compares to the experimental value at 602 nm (Fig. 3f) and is consistent with [5,5] C_{120}-D_{5d}(1). Likewise for isomer II, the calculated UV-vis peak (673.9 nm, Fig. 3h) for [10,0] C_{120}-D_{5h}(10766) is consistent with experimental data (683 nm, Fig. 3i).

A fourth type of characterization for comparing C_{120} structural candidates was Raman. The shaded region (Fig. 3g, Fig. 3j.) indicates metallic character, as predicted for [5,5] tubular carbon and [5,5] C_{120}-D_{5d}(1), (Fig. 3g, see full Raman spectrum, S8). However, a [10,0] tube and [10,0] C_{120}-D_{5h}(10766) should be nonmetallic, which is consistent with the Raman spectrum (Fig. 3j).[18]

For additional characterization, we obtained a STM image (Fig. 5a) that confirmed a tubular shape and aspect ratio consistent with isomer I, [5,5] C_{120}-D_{5d}(1). Using an intermolecular spacing of 0.3 nm from various C_{60} nanostructures, the size of each C_{120} (Isomer I) molecule was determined to be 0.74 nm in diameter and 1.53 nm in length (Figure 1c). See S9 for further details.

We also obtained XPS characterization to analyze the C_{120} carbon content. Fig. 5b shows a symmetric C1s peak with only a trace amount of O1s surface oxygen. This data confirms highly purified carbon samples of pristine [5,5] C_{120} and [10,0] C_{120} fullertubes, *i.e.*, absence of contaminating elements.

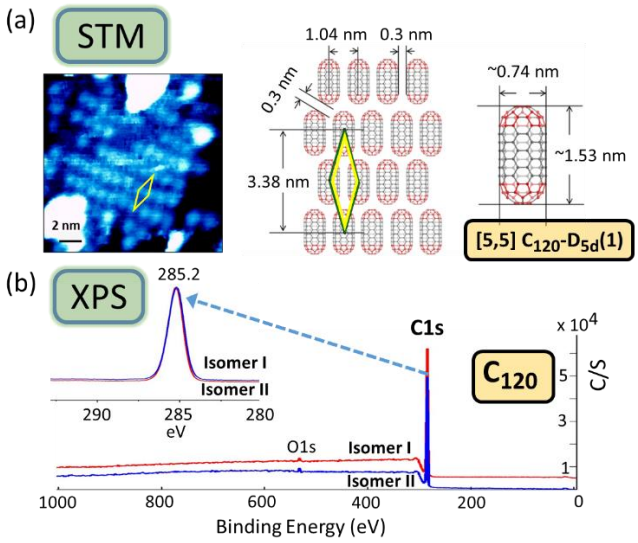


Figure 5. (a) STM of purified isomer I, [5,5] C_{120}-D_{5d}(1), (see S9 for detail on tubular dimensions) and (b) XPS data of isomer I, [5,5] C_{120}-D_{5d}(1) and isomer II, [10,0] C_{120}-D_{5h}(10766)

All the experiments herein represent the seminal characterization for [5,5] C_{120}-D_{5d}(1) and [10,0] C_{120}-D_{5h}(10766). These C_{120} fullertubes are the largest pristine structures of soluble molecular carbon to be isolated. Although an X-ray crystal structure is the usual "gold standard" for structural determination, it requires milligram levels of sample not yet available in this *discovery stage*.

In summary, we have demonstrated that it is possible to use classical analytical instrumentation (with µg sensitivities) to permit structural predictions by comparing experimental data with DFT anisotropic polarizability. The down selection of 10,774 C_{120} IPR isomers to only a *few* tubular candidates renders the [5,5] and [10,0] structural assignments surprisingly facile. Large aspect ratios of fullertubes result in large anisotropic values, which rapidly eliminates 99.9+ % of possible structures. For C_{120}, there were only three tubular IPR candidates with anisotropic polarizabilities greater than 100 Å^3, *e.g.*, 112.1 Å^3, 131.0 Å^3 and 138.5 Å^3. With experimental values of 132.8 Å^3 (isomer I) and 136.4 Å^3 (isomer II), the nearest alternative candidate was C_{120}-D_{5d}(10765), having an anisotropic polarizability of a significantly lower value of 112.1 Å^3, was clearly a mismatch with polarizability and UV-vis. With two C_{120} isomers isolated and two matching candidates, structural assignments were patently obvious.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge at https://pubs.acs.org. Experimental details, isolation procedure using aminopropanol and HPLC, theoretical calculations, and structural information supporting candidate fullertube structures.

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Notes

The authors declare no competing financial interest.

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