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Soluble and Tubular Higher Fullerenes that Encapsulate Metals**

Xing Lu, Takeshi Akasaka,* and Shigeru Nagase*

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Distinctly different from other carbon allotropes, fullerenes are the only soluble form of elemental carbon with a definitive molecular structure.[1] Such properties are fundamentally important, especially for chemists, because isolation of pure isomers and further chemical modification and accurate structural elucidation become possible. At the early stage of fullerene research, however, the structural consideration of fullerenes was a favorite trick of theoreticians.[2] Simple mathematical deduction based on Euler's theorem for polyhedra concludes that exactly 12 pentagons are necessary to form a closed fullerene cage, and the number of hexagons varies with cage size. Whether the isomer occurs in nature or not, the smallest conceivable fullerene is C_{20}, consisting of merely 12 pentagons. To comply with the experimental fact that C_{60} and C_{70} are always the most abundant in soot, the visionary isolated pentagon rule (IPR) was proposed by Kroto, and requires that each of the 12 pentagons are separated by hexagons to avoid high bond strain.[2] Related mathematical works are presented nicely by Fowler and Manolopoulos in "*An Atlas of Fullerenes*", which includes an exhaustive listing of all possible isomers from C_{20} to C_{50} and all IPR isomers between C_{60} and C_{100}.[3] An impressive feature is that the number of isomers, even counting only the ones that obey the IPR, increases dramatically with cage expansion.

In theory, the fullerene regime is infinite, but in reality, the isolated fullerene species are rather limited. The most abundant and certainly the most widely studied fullerene species are I_h-C_{60} and D_{5h}-C_{70} (nomenclature in accordance with Ref. [3]). The structural transition from C_{60} to C_{70} is interesting: the former is cut in half, one half is rotated by 36° relative to the other, then a 10-carbon ring is added in between, and thus C_{70} forms.[4] More interestingly, the D_{5d}-C_{80} isomer (unfortunately no X-ray structure is available) can be grown directly from C_{60} by adding a 20-carbon ring between the two halves, whereas the explicitly elucidated D_{5h}-C_{90} is similarly produced from C_{70} (Figure 1).[5] The tubular appearance of higher fullerenes presents a clear connection with carbon nanotubes and provides valuable clues to the origin of such carbon allotropes.[6]

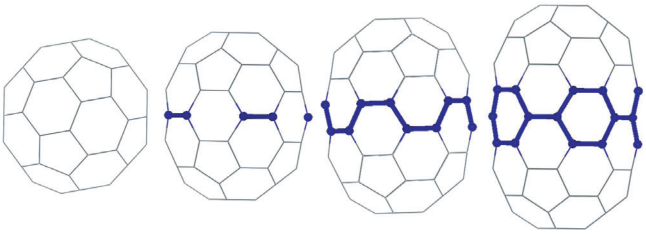

Figure 1. Structures of energetically favorable and truly isolated isomers of C_{60+10n} ($n=0, 1, 2, 3$) showing the tendency of tubular cage expansion. From left to right: I_h-C_{60}, D_{5h}-C_{70}, D_{5d}-C_{80}, and D_{5h}-C_{90}.

In addition to the difficulties of isolating pure samples from numerous possible isomers of higher fullerenes, another main obstacle hindering the acquisition of giant fullerenes is their poor solubility in common solvents, which is associated with their electronic structures, particularly HOMO–LUMO energy gaps. Consequently, concepts based on in situ exohedral modification, (electro)chemical reduction/oxidation, and in situ endohedral metal doping have been invented to alter the electronic structures so as to obtain otherwise insoluble fullerenes. In situ chlorination is effective to acquire small fullerenes with non-IPR structures such as $C_{50}Cl_{10}$, whereas reduction/oxidation afforded only mixtures of giant fullerenes, for example, C_{100}–C_{300}, which remain insoluble after

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[*] Prof. Dr. X. Lu, Prof. Dr. T. Akasaka
Life Science Center for Tsukuba Advanced Research Alliance
University of Tsukuba
Tennodai 1-1-1, Tsukuba, Ibaraki 305-8577 (Japan)
E-mail: akasaka@tara.tsukuba.ac.jp

Prof. Dr. X. Lu
State Key Lab of Materials Processing and Die & Mould Technology
College of Materials Science and Engineering, Huazhong University of Science and Technology (HUST), Wuhan 430074 (China)

Prof. Dr. S. Nagase
Department of Theoretical and Computational Molecular Science
Institute for Molecular Science, Okazaki, Aichi 444-8585 (Japan)
E-mail: nagase@ims.ac.jp

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recovery.[7] Endohedral metal doping therefore appears promising. Recent studies have obtained some of the missing metallofullerenes (La@C_{72}-La@C_{82}), but not large ones.[8]

The recent work by Balch and colleagues makes a big step toward achieving soluble higher fullerenes.[9] They innovatively used chlorobenzene as an HPLC eluent, which has a higher affinity to fullerenes/metallofullerenes than the commonly used toluene, and thereby succeeded in accumulating a fraction containing the large and soluble endofullerenes La_2C_{90} to La_2C_{138}, together with a second series of monolanthanum metallofullerenes with smaller cages and less abundance. Finally, a pure isomer with exactly 100 carbon atoms and two lanthanum centers, $La_2@D_5(450)\text{-}C_{100}$, was isolated and structurally identified with single-crystal X-ray diffraction (Figure 2).

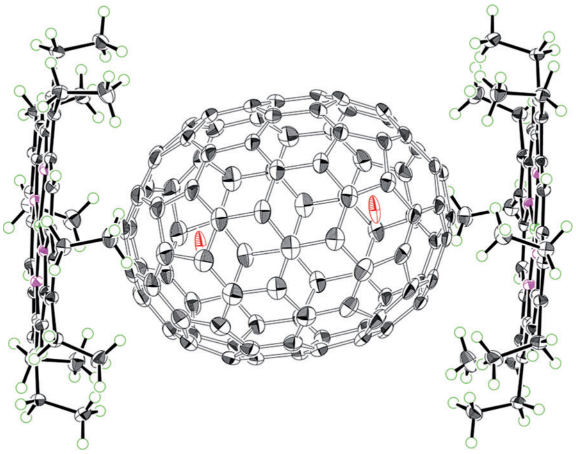

Figure 2. X-ray structure of $La_2@D_5(450)\text{-}C_{100}$ showing its relation to the two surrounding Ni^{II}(OEP) molecules. Thermal ellipsoids shown at 50% probability.

The isolated compound is singular not only because the iconic cage occupies the last entry of the list proposed by Fowler and Manolopoulous,[3] but it also has fascinating structural features. Most of all, its tubular appearance continues to suggest close connection with carbon nanotubes although it departs from the empty fullerene series shown in Figure 1 because of its ionic cage nature. It has been an outstanding observation that endohedral metallofullerenes always bear different cage structures from their corresponding empty fullerenes because of intramolecular electron transfer from the metal to the cage. Several instructive regulations have been proposed to predict the stable isomers of giant fullerenes encaging metals.[10] The X-ray structure of $La_2@D_5(450)\text{-}C_{100}$ complies with the maximal pentagon separation rule proposed by Poblet et al. for regulating the structures of highly charged endofullerenes. In addition, the tubular cage is capped by two Ni^{II}(OEP) molecules (OEP = 2,3,7,8,12,13,17,18-octaethylporphin dianion) in the crystal unit, with its most curved regions interacting in an unexpected way with the planar part of the porphyrins.

Solid evidence has been provided from this work to prove that endohedral metal doping is an effective means to stabilize large fullerenes and possibly to reduce the number of stable isomers. It assumes that pentagons on fullerene cages are preferentially accumulating negative charge transferred from the internal metals and that they must be most separated to avoid strain.[10b] This might also engender the maximal separation of the metal cations which interact strongly with the negatively charged pentagons. $La_2@D_5(450)\text{-}C_{100}$, together with the larger $Sm_2@D_{3d}(822)\text{-}C_{104}$ reported earlier by the same groups,[11] represent the largest cages with X-ray structures. Both show clear tubular shapes and feature long metal–metal distances, but they are "fatter" than the empty fullerene series (see Figure 1). Considering that $Gd_2C_2@D_3(85)\text{-}C_{92}$ encapsulating a planar carbide cluster is even fatter,[12] it seems that the cage shape is highly dependent on the composition of the internal metallic species. In this regard, the triangular metal nitride clusters (e.g. La_3N) might not template tubular higher fullerenes, but more likely round ones.

In conclusion, detection of soluble lanthanum-containing higher fullerenes (La_2C_{90} to La_2C_{138}) opens an avenue to a new scenario in the fullerene community. The tubular appearance of the isolated $La_2@D_5(450)\text{-}C_{100}$ ensures its close kinship with carbon nanotubes, and proves the maximal pentagon isolation rule as well. We have reason to envision future successes in obtaining larger fullerenes, providing brand-new structures, and possibly bringing novel regulations related to metal–cage interplay and formation mechanisms. The metal-enriched electronic configuration and the tubular structure, which enhances charge carrier mobility, together with the solution processable character of such giant fullerene hybrids promise a brilliant future for their use as energy materials.

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