HIGHLIGHT

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Journey to the Holy Grail of a coordination saturated buckyball

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Exohedral metallofullerenes are increasingly gaining attention from both academia and industry due to their unique structural and electronic properties. C_{60} provides an incredible opportunity to bind up to 30 metals on the surface to realize an icosidodecahedral $C_{60}@M_{30}$ supramolecular complex, the Holy Grail of a coordination saturated buckyball. Recently, the Li and Zhan groups reported a rhombicuboctahedral $C_{60}@Cu_{24}$ core−shell structure, a giant leap on their journey toward the Holy Grail.

Since the discovery in 1985,[1] fullerene-C_{60} (C_{60}, buckyball) and its derivatives have always been a research hotspot because of their unique structures and physicochemical properties.[2–17] One particular direction is to exploit the exohedral metallofullerenes,[7–9,18,19] coordination complexes of transition metals (M) spreading over the surface of C_{60} binding to its C=C bonds in η^2 fashion, resulting in various C_{60} derivatives with intriguing photofunctional/electronic properties.[4] As a spherical polyene system, the 30 C=C bonds of C_{60} provide an incredible opportunity to bind up to 30 metal atoms in a μ_{30}-$(\eta^2)_{30}$ fashion and realize the $C_{60}@M_{30}$ core–shell structure, an icosidodecahedral supramolecular complex featuring 20 vertex-shared M_3-trigons, the Holy Grail of a coordination saturated buckyball (Scheme 1).

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Simple as it may seem, the highest nuclearity of the reported exohedral metallofullerenes to date is merely 6,[8,9] including $C_{60}@M_6$ structures with six mononuclear clusters in η^2 fashion (octahedron geometry)[20] and two trinuclear clusters in $(\mu_3-\eta^2:\eta^2:\eta^2)$ fashion.[21] Intuitively, metallofullerenes with nuclearity of more than 6 have been, until now, difficult to synthesize, most likely due to the steric crowding between bulky stabilizing ligands.

One of the key requisites to achieve a coordination saturated buckyball is adopting a vertex-shared M_3-trigon coordination configuration. However, it seems like an impossible mission as the multiple auxiliary ligands surrounding the M_3 unit prevent other M_3 units from hovering over the neighbor hexagons and thus restrict the total number of M_3 units on the C_{60} surface, particularly for these open-shell transition metals with a coordination number no less than 4.

The studies of metallofullerenes can be dated back to the early 1990s, when several metal-coated fulleride clusters with high nuclearity such as $C_{60}@Li_{12}$,[22,23] $C_{60}@Ba_{32}$, $C_{60}@Ca_{32}$,[24]

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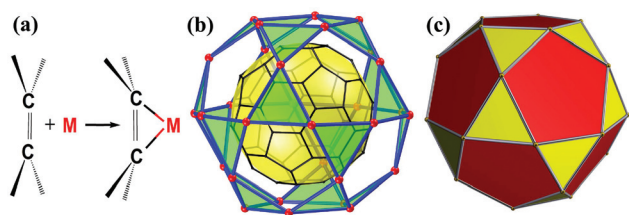
Scheme 1 Formation of η^2-fashion metal-olefin complex (a), the proposed icosidodecahedral $C_{60}@M_{30}$ structure in a μ_{30}-$(\eta^2)_{30}$ coordination mode (b), and the icosidodecahedron polyhedron (c). For clarity, the coordination interactions between M and C=C are omitted in (b).

and others[25,26] were speculated to exist under specific conditions. *Ab initio* molecular dynamics calculation revealed that $C_{60}@Li_{12}$ could be a stable cluster. However, their exact structures were not confirmed due to the lack of analytical techniques, preventing further investigation of their functions.

Recently, Li's group at Jinan University and Zhan's group at Shantou University jointly reported a rhombicuboctahedral $C_{60}@Cu_{24}$, a metallofullerene of unprecedented high nuclearity.[27] It is a giant leap toward complete coordination on the C_{60} surface. Overall, the ingenious strategies in their endeavor toward high nuclearity include: (i) adopting closed-shell Cu(I) with a lower coordination number instead of open-shell metals and (ii) adopting anionic bridge ligands instead of terminal ligands. Both of these strategies were intended to minimize the steric crowd of the M_3 coordination sphere. As a continuous effort of the two research groups to explore metallofullerene complexes, four exohedral Cu(I)–C_{60} (cuprofullerene) carboxylate complexes with nuclearities of 6, 12, and 24 were successfully synthesized by solvothermal reactions of fluorocarboxylic/bicarboxylic acid, Cu_2O, and C_{60} in aromatic solvents. From a structure perspective, all of the cuprofullerene complexes embody the same coordination mode of $[\mu_3-\eta^2:\eta^2:\eta^2)$-$C_{60}]$-$Cu_3$-$[(\mu_2-\kappa^1:\kappa^1)$-COO]$_3$ (Fig. 1a) with a $Cu_3 : C_{60}$ ratio of $2:1$, $4:1$, and $8:1$ (Fig. 1b–d). Particularly, the 24-nuclear cuprofullerene represents a rhombicuboctahedral $C_{60}@Cu_{24}$ core–shell structure with 8 Cu$_3$ units canopying on
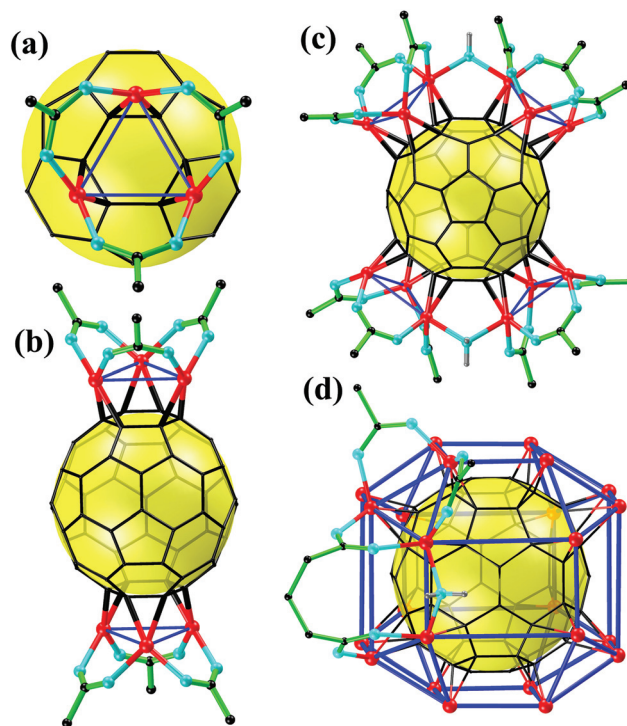

Fig. 1 The simplified structures of the synthesized cuprofullerenes. (a) Cu$_3$ unit, (b) $C_{60}@Cu_6$, (c) $C_{60}@Cu_{12}$ and (d) $C_{60}@Cu_{24}$. Color code: red, Cu; cyan, O; black, C; green, F; gray, H.

the 8 independent hexagons of C_{60} (Fig. 1d), paving the road toward the completely coordinated C_{60}. For detailed structural analysis, please refer to their recently published paper.[27]

As opposed to the reported exohedral M_3-metallofullerenes, in which the monodentate auxiliary ligands such as phosphine, CO, and isocyanide were frequently used,[7–9] the synergistic associations of $(\mu_2-\kappa^1:\kappa^1)$-carboxylate and $(\mu_3-\eta^2:\eta^2:\eta^2)$-hexagon could significantly enhance the stability of the Cu$_3$ units. Furthermore, the low coordination of Cu(I) and the outward orientation of carboxylates far away from the buckyball could endow the Cu$_3$ unit with much relieved steric crowd-

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ing on the surface of C_{60}, which provides an opportunity to squeeze in more Cu_3 units on the adjacent hexagons to increase the overall nuclearity.

Besides adopting low coordination Cu(ɪ) and carboxylate as auxiliary ligands, the use of fluorocarboxylate as ligands might also play an essential role in the formation of cuprofullerene complexes of high nuclearity. Compared with the non-fluorinated carboxylate, the poorly coordinated fluorocarboxylate facilitates relatively strong association of the weak basic olefin C_{60} with Cu(ɪ), as reported in the tris(η^2-ethene)-Cu(ɪ) cationic complexes.[28] As a matter of fact, using non-fluorinated n-butyl-carboxylate under similar conditions did not produce a complex of similar nuclearity. Inspired by the successful evolution of nuclearity from $C_{60}@Cu_6$ to $C_{60}@Cu_{12}$ through increasing the concentration of heptafluorobutyrate auxiliary ligands, the $C_{60}@Cu_{24}$ structure was eventually realized by using dicarboxylate, hexafluoroglutarate and glutarate, as bridging ligands, which is vital to further increase the local concentration of carboxylates around the surface of the buckyball. As a result, the bridging dicarboxylate provides extra bridging interactions beyond μ_2-H_2O associating eight Cu_3 units, further stabilizing the rhombicuboctahedral $C_{60}@Cu_{24}$ core–shell structure. It is worth pointing out that the authors were also able to obtain the extremely high-nuclear structure with non-fluorinated glutarate in 1-chloronaphthalene, in which the high solubility of C_{60} might have played an important role. It exemplifies the intricacy and complexity of the crystallization process, which leads us to believe that the final mission, the complete coordination of C_{60}, can be accomplished by the fine tuning of the reaction systems. In addition, by closely looking into the geometry of the obtained $C_{60}@Cu_{24}$ molecule, it appears there is enough space above the 6 vacant C=C bonds to allow additional metal atoms and complete the proposed $C_{60}@Cu_{30}$ icosidodecahedron, provided the suitable auxiliary ligands are used. We look forward to the realization of the great Holy Grail by the authors as soon as possible.

Note that solvothermal conditions were utilized for the first time to prepare exohedral metallofullerene in this work. The high-boiling-point aromatic solvents make it possible to run the solvothermal reactions at rather high temperatures, and thus to overcome the energy barriers toward these high-nuclear cuprofullerenes.

The initial photophysical/photochemical properties were studied for the above-obtained Cu_3-metallofullerenes. Their solid-state UV-Vis diffuse reflectance spectra exhibit absorption of the whole UV-visible area, indicating more efficient absorption of visible light than the pristine C_{60} due to the complexation of Cu(ɪ). Theoretical calculations confirmed that the complexation could reduce the symmetry and disturb the π-system of C_{60}, resulting in the symmetry-allowed excitation in the visible-light region. With the increase of nuclearity, the lowest absorptions of the four complexes show a hypsochromic shift, suggesting the potential influence of nuclearity on their electronic structures. Compared with the pristine C_{60} material, the cuprofullerene complexes show not only much higher efficient absorption of visible light, but also more controllable HOMO–LUMO gap, which implies an attractive prospect in utilizing solar energy.

As organocopper reagents, we could also expect these cuprofullerene complexes to function as novel catalysts in preparing organic fullerene derivatives,[29] opening a new door for organic fullerene chemistry.

Conclusions

In short, the Li and Zhan groups have successfully prepared a series of exohedral cuprofullerene complexes, featuring Cu_3 units canopying on the C_{60} surface in a (μ_3–η^2:η^2:η^2) fashion, by judiciously selecting fluorocarboxylate/dicarboxylate as auxiliary ligands and solvothermal reaction conditions. The ratio of $M_3 : C_{60}$ has been expanded from 2 : 1 to 4 : 1 and 8 : 1, forming the unprecedented 12- and 24-nuclear cuprofullerenes. Particularly, the 24-nuclear complex, a rhombicuboctahedral $C_{60}@Cu_{24}$ core–shell structure, represents an exohedral metallofullerene of the most nuclearity, a giant leap toward the coordination saturated $C_{60}@M_{30}$. This work greatly enriches the structural diversity of exohedral metallofullerenes and is expected to bring advanced applications such as in the photoelectric conversion and catalytic synthesis of organic fullerene derivatives. We look forward to the realization of $C_{60}@M_{30}$ icosidodecahedron and its intriguing applications in the near future.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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