Communication

# Exohedral Cuprofullerene: Sequentially Expanding Metal Olefin Up to a C60@Cu24 Rhombicuboctahedron

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# Exohedral Cuprofullerene: Sequentially Expanding Metal Olefin Up to a $C_{60}@Cu_{24}$ Rhombicuboctahedron

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Supporting Information Placeholder

ABSTRACT: Exohedral cuprofullerenes with 6-, 12-, or 24-nuclearity were obtained by utilizing fluorocarboxylic/dicarboxylic acid under solvothermal conditions. The 24-nuclear molecule presents a $C_{60}@Cu_{24}$ core-shell structure with a rhombicuboctahedron $Cu_{24}$ coated on the $C_{60}$ core, representing the highest nuclearity in metallofullerene. The resultant complexes show an efficient absorption of visible light as opposed to the pristine $C_{60}$. TD-DFT calculations revealed the charge transfer from Cu(I) and O atoms to fullerene moiety dominate the photophysical process.

Since the first $C_{60}$-Pt complex $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$ was reported in 1991,[1] numerous exohedral metallofullerenes have been explored not only because of the extraordinary binding capabilities of fullerenes for transition metals (M) in hapto fashion but also their novel properties and potential applications.[2-5] Compared with the vast number of exohedral metallofullerenes with open-shell metals (group 6-10),[2-5] only 12 examples containing closed-shell Cu(I)/Ag(I)/Au(I) (two Cu(I)-,[6-7] seven Ag(I)-,[7-11] and three Au(I)-structures[7, 12]) have been reported so far, and most of them are assembled from organic fullerene derivatives. On the other hand, various Cu(I)/Ag(I)/Au(I)-olefin complexes[13-17] including tris($\eta^2$-ethene)-Cu(I)/Ag(I)/Au(I) cationic complexes[18-20] have been prepared, suggesting high binding abilities of olefin for Cu(I)/Ag(I)/Au(I) atoms. In fact, the convex $C_{60}$ renders more favorable geometry for binding metal in $\eta^2$-fashion than planar ethene molecule[5] (Scheme 1a).

As a spherical polyene system, 30 C=C in $C_{60}$ provide an incredible possibility to bind 30 metal atoms in a saturated $\mu_{30}\text{-}(\eta^2)_{30}$ fashion to complete a $C_{60}@M_{30}$ icosidodecahedron with 20 vertex-shared $M_3$-trigons (Scheme 1b). Up to now, the highest nuclearity is 6 in the reported exohedral metallofullerenes, such as 6:1 products through six $\eta^2$- or $\eta^2/\eta^5$-interactions,[21-23] and 2:1 adducts through double $(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2)$-interactions.[24-25] It seems an impassable task to fulfill the saturated fashion using open-shell metals, because these metals show coordination number no less than 4, and the bulky steric crowd caused by the multiple auxiliary ligands will prevent more $M_3$ being coated on the neighbor hexagons and restrict the number of $M_3$ on $C_{60}$ surface, in spite of

numerous examples of $(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2)$-metallofullerenes.[5] Therefore, minimizing the steric crowd surrounding the $M_3$, for example, adopting the closed-shell Cu(I) with low coordination number (no more than 4) and anionic bridge ligands but not terminal ligands, are believed to be effective strategies to achieve a high nuclear metallofullerene.

Scheme 1. Formation of $\eta^2$-fashion metal-olefin complex to show the convexity of olefin (a) and the proposed $C_{60}@M_{30}$ icosidodecahedron to show a $\mu_{30}\text{-}(\eta^2)_{30}$ coordinating $C_{60}$ (b).
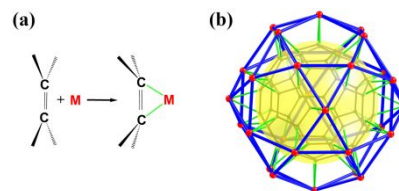


Polynuclear Cu(I)-olefin fluorocarboxylate have been explored for several decades,[15, 26-27] in which two Cu(I) are bridged by a $(\mu_2\text{-}\kappa^1{:}\kappa^1)$-carboxylate and the $\eta^2$-C=C binds on one Cu(I) atom. Prompted by these results, four exohedral Cu(I)-$C_{60}$ (cuprofullerene) carboxylate complexes from hexa-, dodeca- to icositetra-nuclearity were prepared with fluorocarboxylic/dicarboxylic acid, $Cu_2O$ and $C_{60}$ (Figures 1 and S1, Scheme S1) under solvothermal conditions in aromatic solvents (details in SI), similar to the synthesis of the disk-type coordination nano-Saturn complexes.[28] They show the essential $Cu_3\text{-}[(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2)\text{-}C_{60}]$ structure (Figure 2a) with evolution of $Cu_3{:}C_{60}$ ratio from 2:1, 4:1 to 8:1 (Figures 1 and S3). Noteworthily, the 24-nuclear cuprofullerene shows a $C_{60}@Cu_{24}$ core-shell rhombicuboctahedron with eight $Cu_3$ units coated on the 8 independent hexagons of the $C_{60}$ surface. The complexation of Cu(I) atoms enhances the efficient absorption of visible light than $C_{60}$ itself. These results realize the first $\eta^2$-cuprofullerene complex and the highest nuclearity of metallofullerene. Their crystalline phase purity was ensured by powder X-ray diffraction (PXRD) analysis (Figure S2). Unfortunately, they are decomposed in common solvents, which restricts the exploration of their properties in solution.

All the four complexes are based on a $Cu_3$ unit (Figures 1 and 2a) synergistically associated by three $(\mu_2\text{-}\kappa^1{:}\kappa^1)$-carboxylate and one $(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2)$-hexagon of $C_{60}$. The Cu···Cu distances are 3.21~3.40 Å, and the C–Cu about 1.98~2.06 Å (Tables S2-5), similar to that in the Cu(I)-olefin carboxylate[27] but slightly shorter than C−M (2.20-2.30 Å) in other exohedral metallofullerenes.[5] The C=C (1.43 to 1.45 Å) and C−C (1.48~1.50 Å) lengths of the coordinated hexagons are slightly longer than that (1.38~1.40 Å and 1.42-1.44 Å) in pristine $C_{60}$. The remaining coordination sites of the Cu(I) atoms are vacant or weakly coordinated by terminal/bridging $H_2O$/carboxylic molecules with Cu−O lengths of 2.16~2.41 Å (Figures 1-2). The maxima outer size of the cuprofullerenes are larger than 2.0 nm, implying a nanosized cuprofullerene molecule.
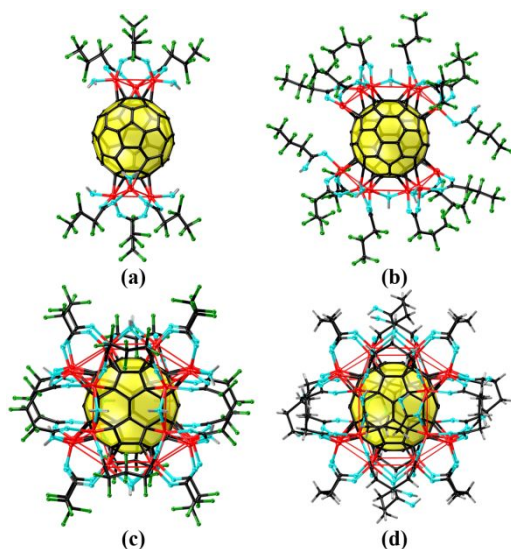


**Figure 1.** Molecular structures of the cuprofullerene **$Cu_6$** (a), **$Cu_{12}$** (b) **$Cu_{24}$** (c) and **$Cu_{24}$-H** (d) in the four complexes. (Color code: red, Cu; cyan, O; black, C; green, F; gray, H)

It is believed that the stability of the $Cu_3$ units can be enhanced by the synergistical associations of the $(\mu_2\text{-}\kappa^1{:}\kappa^1)$-carboxylate and $(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2)$-hexagon significantly, as opposite to other $M_3$-metallofullerenes with monodentate auxiliary ligands such as phosphine and CO.[24-25] Furthermore, the $Cu_3$ unit shows much small steric crowd due to the low coordination number (3 or 4) of Cu(I) atoms and the outward orientation of carboxylate, providing a possibility that more $Cu_3$ units can be coated on the adjacent hexagons of the $C_{60}$ to expand the nuclearity.

The hexanuclear complex **1** (**$Cu_6$**) is crystallized in a high symmetrical *R*-3m space group (Table S1) with heptafluorobutyrate as auxiliary ligand. It shows the first *trans* bis-adduct hexanuclear metallofullerene[24-25] based on pristine $C_{60}$. The fourth coordination site of each Cu(I) atom is further occupied by a terminal $H_2O$ with Cu−O distance 2.1642(9) Å (Figure 1a and Table S2).

Doubling the concentration of heptafluorobutyric acid results in a cocrystal (complex **2**) of dodecanuclear cuprofullerene (**$Cu_{12}$**, Figure 1b) and mononuclear $Cu(H_2O)_4(C_3F_7COO)_2$ molecules. In the **$Cu_{12}$** molecule, four $Cu_3$ units are coated on the $C_{60}$ surface, in which two adjacent $Cu_3$ units are bridged by a $\mu_2\text{-}H_2O$ with $d_{Cu-O}$ 2.2198(2) and 2.2498(2) to form a $Cu_3\text{-}(\mu_2\text{-}H_2O)\text{-}Cu_3$ unit (Figures 1b, 2b and Table S3). Two terminal $H_2O$ are attached on two another Cu(I) atoms with $d_{Cu-O}$ 2.2152(2) and 2.2115(2) Å. A

neutral terminal $C_3F_7COOH$ molecule is furtherly coordinated to the third Cu(I) atom of one $Cu_3$ unit with C=O but not C−OH, in which the coordinated CO shows a typical C=O distance (1.1944(1) Å) and another CO distance is 1.3047(1) Å (Table S3). The centrosymmetrical molecule shows a pair of symmetry-dependent $Cu_3\text{-}(\mu_2\text{-}H_2O)\text{-}Cu_3$ (Figure 2b) coated on the $C_{60}$ surface in a *trans*-fashion.[24] The mononuclear Cu(II)-coordination molecule and chlorobenzene molecule are co-crystallized to occupy the vacant space among the cuprofullerene molecules (Figure S5).
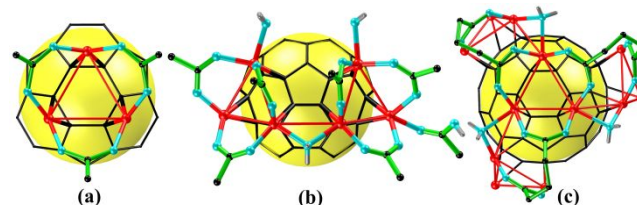


**Figure 2.** The structural units of the cuprofullerenes. (a) The $Cu_3$ unit doubly-bridged by $(\mu_2\text{-}\kappa^1{:}\kappa^1)$-carboxylate and $(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2)$-hexagon. (b) The $Cu_3\text{-}(\mu_2\text{-}H_2O)\text{-}Cu_3$ unit. (c) The multi-$Cu_3$ units doubly-bridged by $\mu_2\text{-}H_2O$ and $(\mu_4\text{-}\kappa^1{:}\kappa^1{:}\kappa^1{:}\kappa^1)$-glutarate. (Color code: red, Cu; cyan, O; black, C; gray, H)

Hexafluoroglutaric acid results in a 24-nuclear cuprofullerene molecule with 8 $Cu_3$ coated on the 8 alternate but not fused hexagons (complex 3, **$Cu_{24}$**, Figure 1c). Any two adjacent $Cu_3$ are doubly-bridged by one $\mu_2\text{-}H_2O$ and one $(\mu_4\text{-}\kappa^1{:}\kappa^1{:}\kappa^1{:}\kappa^1)$-hexafluoroglutarate (Figure 2c). Accordingly, the 8 $Cu_3$ units form a large Archimedean rhombicuboctahedron coated on the Archimedean truncated icosahedron in a $\mu_{24}\text{-}(\eta^2)_{24}\text{-}C_{60}$ fashion to construct a $C_{60}@Cu_{24}$ core-shell structure, leaving the 6 C=C bonds vacant in the position of an octahedral vertex (Figures 1c and 3a). Two 24-halogenated $C_{60}$-derivatives ($C_{60}X_{24}$, X = Cl, Br) rhombicuboctahedron were reported by Troyanov et al, however, in which as high as 18 C=C bonds are remained.[29-31]

Another 24-nuclear cuprofullerene similar to complex 3 was also obtained using non-fluorinated glutaric acid in chloronaphthalene (complex 4, **$Cu_{24}$-H**). It is crystallized in *R*-3 space group. Different from the structure of **$Cu_{24}$**, the position of a pair $\mu_2\text{-}H_2O$ is occupied by the O atom from C=O but not C-OH of a neutral glutaric acid (Figure 1d). The coordinated CO shows much shorter lengths (1.2430(3) Å) than the unbound CO group (1.3438(3) Å), similar with that in the **$Cu_{12}$** molecule. The neutral glutaric acid shows a $(\mu_4\text{-}\kappa^2{:}\kappa^2)$-bridge fashion across the vacant C=C (Figure 1d).
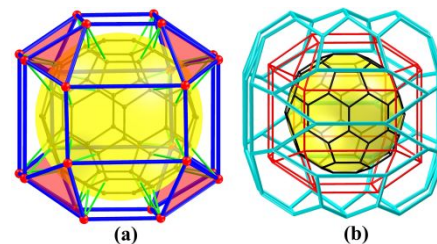


**Figure 3.** (a) Illustration of the $C_{60}@Cu_{24}$ core-shell structure showing the $Cu_{24}$ rhombicuboctahedron (red ball and blue stick) coated on the $C_{60}$ core (yellow ball). (b) The triple-sphere $C_{60}@Cu_{24}@O_{60}$ structure showing the $C_{60}@Cu_{24}$ (red-black-yellow) within the fullerene-like $O_{60}$ cage (cyan).

Interestingly, a total of 60 coordinating O atoms in the **$Cu_{24}$/$Cu_{24}$-H** molecule exhibits a fullerene-like $O_{60}$ outermost

sphere,[32] which encapsulates $C_{60}@Cu_{24}$ to form a fascinating triple-sphere $C_{60}@Cu_{24}@O_{60}$ core-shell structure (Figure 3b).

Fluorocarboxylate ligands play an essential role in the formation of the cuprofullerene complexes. Compared with the nonfluorinated carboxylate, the poorly coordinating fluorocarboxylate facilitate the association of the weak basic olefin $C_{60}$ with Cu(I) atoms.[20] In fact, similar cuprofullerene complexes were not obtained using nonfluorinated $n$-butylcarboxylate. The synergistical bridging coordination of the anionic carboxylate not only enhance the stability of the $Cu_3$ units, but also reduce the steric crowd around the $Cu_3$ units. Consequently, two $Cu_3$ units can be bridged on the adjacent hexagons by one $\mu_2$-$H_2O$ to form the dodecanuclear cuprofullerene based on $Cu_3$-($\mu_2$-$H_2O$)-$Cu_3$ through increasing the concentration of heptafluorobutyric acid. Accordingly, it seems that each $Cu_3$ can be bridged with three $Cu_3$ by three $\mu_2$-$H_2O$ molecules to form a structure of $(Cu_3)_8(\mu_2$-$H_2O)_{12}$ coated on the $C_{60}$. Further increasing the concentration of the monocarboxylic acid did not give $C_{60}@Cu_{24}$, however, it was realized by using hexafluoroglutarate/glutarate. The flexible dicarboxylate provides extra bridging interactions beyond $\mu_2$-$H_2O$ to associate eight $Cu_3$ units, further stabilizing the $C_{60}@Cu_{24}$ rhombicuboctahedron. Even the nonfluorinated glutarate can generate the extremely high nuclear cuprofullerene in 1-chloronaphthalene, in which $C_{60}$ shows high solubility.

Unfortunately, the proposed $C_{60}@Cu_{30}$ icosidodecahedron constructed by 20 $Cu_3$-trigons with the shared Cu vertex (Scheme 1b) has not been obtained, though $Cu_{30}$ icosidodecahedron have been widely reported.[33-34] Great efforts have been made to fulfill the remaining C=C but to no avail until now. It is reasonable that the ($\mu_2$-$\kappa^1$:$\kappa^1$)-carboxylate and the coordination geometry of Cu(I) to form the independent $Cu_3$ rather than poly-$Cu_3$ with shared vertex, which indicates only 8 independent hexagons in $C_{60}$ can be coated by 8 $Cu_3$ units mostly to complete the $C_{60}@Cu_{24}$ rhombicuboctahedron.

Solid-state UV-Vis diffuse reflectance spectra of complexes **1-4** cover almost the whole UV-visible range (Figure 4a), indicating a more efficient absorption of visible light due to the complexation of Cu(I) than the pristine $C_{60}$. The complexation reduces the symmetry and disturbs the $\pi$-system of $C_{60}$, leading to the allowed absorptions of visible light,[5] which is forbidden on electronic transition in pristine $C_{60}$ molecule. With the nuclearity increasing in the four complexes, the lowest absorptions show a hypsochromic shift, indicating the influence of nuclearity on their electronic structures.

In order to deeply understand the possible photophysical mechanism, TD-DFT calculations were performed (Theoretical Calculation Details in SI). The calculated lowest absorption energy are 2.41 eV (514 nm), 2.44 eV (507 nm), 2.53 eV (488 nm) to 2.59 eV (479 nm) for the $\mathbf{Cu_6}$, $\mathbf{Cu_{12}}$, $\mathbf{Cu_{24}}$ and $\mathbf{Cu_{24}}$-H molecules respectively, much lower than that (3.77 eV, 328.92 nm) of $C_{60}$ molecule (Figures 4, S14 and Tables S6-7), consistent with the experimental results. More than one vertical transition is responsible for the absorptions. EDD maps of the major vertical transition states (oscillator strength $f > 0$) suggest the lowest absorptions are dominated by the charge transfer of (Cu(I), O) $\rightarrow$ fullerene and $\pi \rightarrow \pi^*$ within the fullerene with a very little contribution of F atoms, more complicated than that in $C_{60}$ molecule. Carefully examining the orbital contributions for the major transition states (Table S7) and the calculated atom contributions for the involved frontier molecular orbitals (Table S8) we found that the contributions of Cu atom increase slightly on both the occupied frontier orbitals (from near 30% to 40%) and the

unoccupied (from near 10% to 30%) with the increasing of the nuclearity. While the contributions of $C_{60}$ on the frontier orbitals decrease slightly, and O atoms show almost constant contributions. These results suggest that the contributions of Cu $\rightarrow$ fullerene and Cu $\rightarrow$ Cu are enhanced upon the increasing of the nuclearity, which may cause the hypsochromic shift of the absorptions. Accordingly, the significant enhancement of the absorption efficiency for visible light suggest that these cuprofullerene complexes can be a candidate for photofunctional materials.
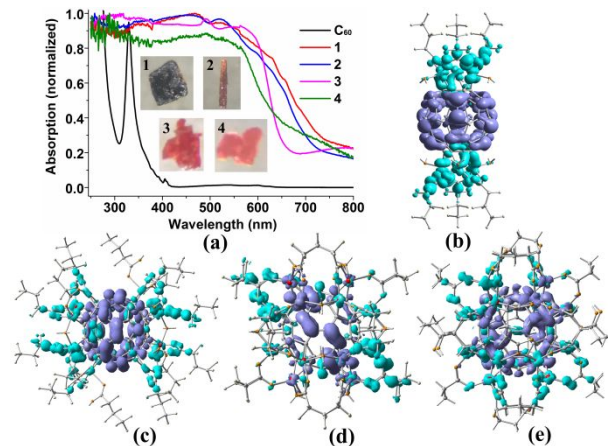


**Figure 4.** (a) The UV-Vis spectra of $C_{60}$ and the complexes **1-4** with inset crystal photographs. (b-e) The calculated electron density difference (EDD) maps (density transferring from the parts in cyan to purple, isovalue = 0.0004 a.u.) of the selected vertical singlet excited states ($f > 0$) with the lowest energy gap for the $\mathbf{Cu_6}$ (b, $S_{11}$), $\mathbf{Cu_{12}}$ (c, $S_9$), $\mathbf{Cu_{24}}$ (d, $S_{11}$) and $\mathbf{Cu_{24}}$-H (e, $S_{11}$) molecules.

In conclusion, four multinuclear exohedral cuprofullerene complexes have been successfully prepared, featuring trinuclear $Cu_3$ units canopying on the $C_{60}$ surface in a ($\mu_3$-$\eta^2$:$\eta^2$:$\eta^2$)-fashion. Assisted by fluorocarboxylate/dicarboxylate, the ratio of $Cu_3$:$C_{60}$ can be expanded from 2:1, 4:1 to 8:1 to form nanosized 6-, 12- and 24-nuclear cuprofullerenes. The 24-nuclear molecule presents not only the most nuclearity of exohedral metallofullerene, but also a $C_{60}@Cu_{24}$ rhombicuboctahedron. TD-DFT calculations revealed the complexation can significantly increase the absorption efficiency of visible light compared with the pristine $C_{60}$ molecule, and the dominating charge transfer from Cu(I) and O atoms to fullerene moiety should be responsible for the much improved absorptions. This work greatly enriches the structural diversity of exohedral metallofullerene family. It also provides a new direction for the design of fullerene-related materials with enhanced absorption efficiency of visible light. Studies to fulfill saturated coordination on $C_{60}$ are ongoing and we expect their applications as photofunctional materials in the future.

## ASSOCIATED CONTENT

### Supporting Information

Experimental and characterization details; additional images and figures; PXRD patterns; UV-Vis spectra; TGA analysis; Calculation details; Crystallographic data for the four complexes (CIF)
The Supporting Information is available free of charge on the ACS Publications website.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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**Notes**

The authors declare no competing financial interests.

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SYNOPSIS TOC

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