

Theoretical Investigation on Icosahedral $C_{60}(FeCp)_{12}$: A Hybrid of C_{60} and Ferrocene

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A perfect hybrid complex $C_{60}(FeCp)_{12}$ is predicted using density functional theory method. This fullerene derivative could be viewed as a C_{60} cage of which each C_5 ring coordinates a (FeCp) ligand. Theoretical calculation reveals that it has a large lowest unoccupied molecular orbital–highest unoccupied molecular orbital gap (2.53 eV) and keeps the I_h symmetry of C_{60} . But the C–C bond length of its inner C_{60} cage tends to be uniform, which is quite different from the bonding character of C_{60} fullerene. Further investigation reveals that the chemical bonding, TDOS and the aromaticity of the (C_5FeCp) unit in $C_{60}(FeCp)_{12}$ are similar as those of ferrocene molecule, which indicates the similarity of their electronic properties. So,

this compound could be viewed as the combination of ferrocene molecules. Thus, its unconventional formation process from 12 $Fe(Cp)_2$ is proposed and the reaction energy is calculated. As the $C_{60}(FeCp)_{12}$ compound has the geometry framework as C_{60} and the electronic characters as ferrocene, it would inherit the outstanding properties from both two molecules and have wide potential applications in nanochemistry. We hope our study could give some references for the further investigation and experimental synthesis research of the $C_{60}(FeCp)_{12}$ compound. © 2015 Wiley Periodicals, Inc.

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Introduction

Since first reported in 1991, fullerene (I_h-C_{60}) has attracted much attention of researchers.^[1–3] It is a spherical molecule composed of 12 pentagonal and 20 hexagonal faces, which contains a 60 π -electrons delocalized system.^[4] Because of its great diversity of chemical reactivity, fullerene has superior capability to coordinate metal atoms outside carbon cage to form organometallic compounds.^[3,5–18] The different coordination modes (from η^1 to η^6) have been reviewed by Soto group,^[19] of which η^2 and η^5 hapticity are the main modes.^[20–27] Ferrocene ($Fe(Cp)_2$) is another “star molecule” of the 20th century. It is first reported by Kealy^[28] and Miller^[29] in 1950s, then researchers reveal that it has the special sandwich structure containing a metal- π bonding system.^[30–33] As there are pentagonal carbon arrays in both C_{60} and ferrocene molecules, an intriguing idea of synthesizing their hybrid complex through face-to-face fusion arises much interests.

The η^5 hybrid complexes $C_{60}MCp^+$ ($M = Fe, Ru, Os$) have been first reported by Chistyakov group^[34] using quantum-chemical calculation. Theoretical investigation reveals that these complexes have the similar structure as ferrocene which also contain the metal- π system, but their sandwich structures are built on the C_{60} framework. As a result, this kind of compounds would inherit the outstanding properties from both C_{60} and ferrocene molecules. Soon after that, other similar sandwich-fullerene η^5 complexes have been reported theoretically.^[35–43] Meanwhile, great efforts are made for studying the experimental synthesis of this kind of complexes. A series of work are reported by Nakamura and coworkers^[44–48] on the synthesizing process of $Fe(C_{60}Me_5)Cp$, which is named “bucky ferrocene.”^[39] In the reaction, fullerene derivatives are used as the Cp-type ligand precursor, then they react with the $[FeCp(CO)_2]_2$ or its

analogues at the high temperature to gain the hybrid products. This new synthetic method is illuminating. Then, lots of studies are carried on synthetic route of bucky ferrocene^[49–56] and their structures are investigated theoretically.^[57–61]

As there is a stable π system in fullerene, when coordinating the organometallic ligands the delocalized π system should be broken, which indicates a high-energy barrier. As a result, the formation process of bucky ferrocenes is usually complicated. The C_{60} cage in the products would lose its perfect I_h symmetry and contain other organic substituents. In this study, we predict a perfect bucky ferrocene with high symmetry. As the C_{60} molecule contains 12 pentagonal carbon arrays in its structure, it would be possible that each pentagonal unit coordinates a (FeCp) ligand to form the $C_{60}(FeCp)_{12}$, which may keep the I_h symmetry.^[62,63] What is more, this bucky fullerene could be viewed as a composition of 12 $Fe(Cp)_2$ molecules from its structure, which offers another possible synthetic route for $C_{60}(FeCp)_{12}$ from ferrocene molecules. As a perfect hybrid of C_{60} and ferrocene, the structure and properties of this compound could be quite different from the conventional bucky ferrocene which is synthesized from the C_{60} framework. It would better

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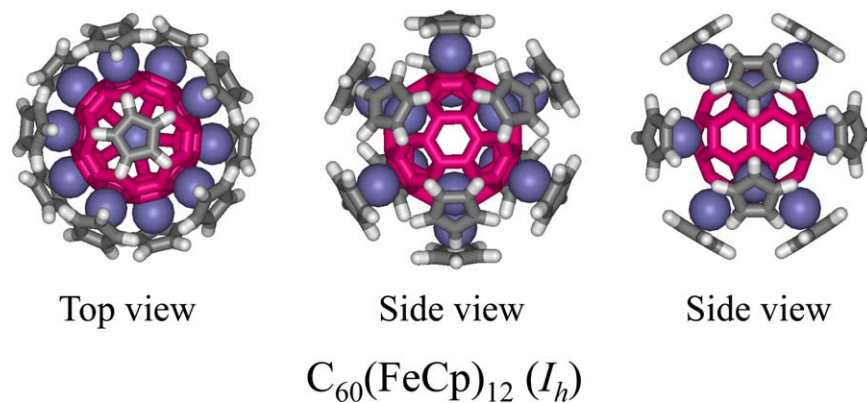


Figure 1. Top view and two side views of optimized molecular structure for $C_{60}(FeCp)_{12}$ at TPSS/6-31G*/LanL2DZ level (Fe in CPK model, C and H in stick model), symmetry of the complex is labeled below the structure.

inherit the rich chemical and physical characters from both C_{60} and ferrocene. So in the following parts, we analysis the geometry and electronic structure of the $C_{60}(FeCp)_{12}$ complex, and discuss its possible formation process from 12 $Fe(Cp)_2$ molecules.

Computational Details

TPSS functional^[64] of density function theory (DFT), which is proved to be reliable for investigating the transition metal system,^[65] is chosen for the theoretical study in this article. All the geometry optimizations are using mixed basis sets (6-31G*

for hydrocarbon and LanL2DZ for Fe atom). The vibrational frequencies are checked to ensure the stability of the compounds at the same theoretical level. To gain insight into the stability of the $C_{60}(FeCp)_{12}$, the energy and energy gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital (HOMO–LUMO gap) are calculated using the same mixed basis sets. Adaptive natural density partitioning (AdNDP) method^[66,67] is implemented to analyze the bonding pattern of the complexes. All calculations are performed using the Gaussian 09 package^[68] and molecular orbitals (MO) visualization is performed by Molekel 5.4.^[69]

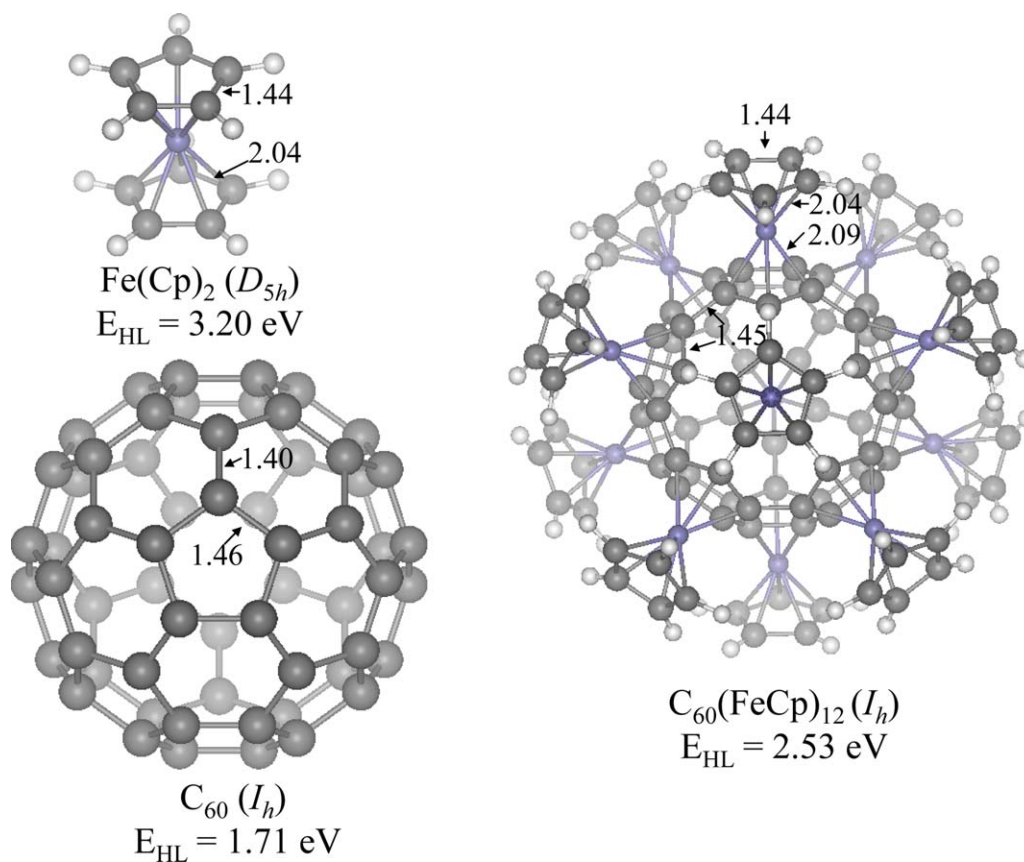


Figure 2. Optimized molecular structures of the $Fe(Cp)_2$, C_{60} , and $C_{60}(FeCp)_{12}$ complexes at TPSS/6-31G*/LanL2DZ level. Symmetry, HOMO–LUMO gap (E_{HL}), and bond-length (in angstrom) at the same level are marked below each structure (Fe in purple, C in dark gray, and H in light gray).

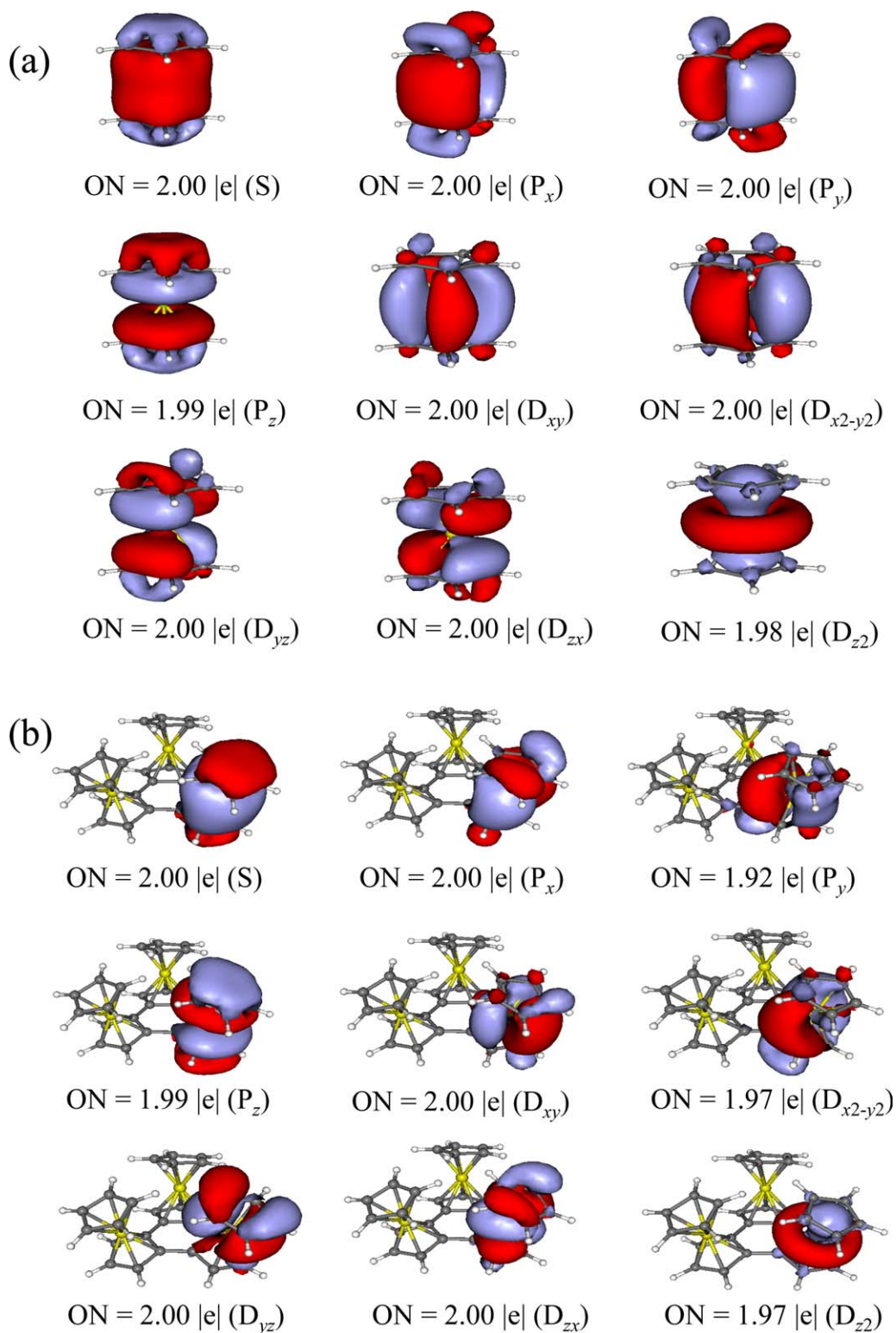


Figure 3. AdNDP chemical bonding of a) Fe(Cp)₂ and b) C₆₀(FeCp)₁₂, occupation numbers are labeled below (Fe in yellow, C in dark gray, and H in light gray).

Results and Discussion

Structure and stability

The geometry structure of C₆₀(FeCp)₁₂ is built and optimized from the ideal *I_h* symmetry. As shown in Figure 1, the com-

pound keeps the perfect *I_h* symmetry after optimization under the TPSS/6-31G*/LanL2DZ level. In this local minimum structure, the Cp ligands and the pentagonal faces of the inner C₆₀ cage are in the eclipsed position. But as ferrocene, the C₆₀(FeCp)₁₂ molecule has another staggered configuration.

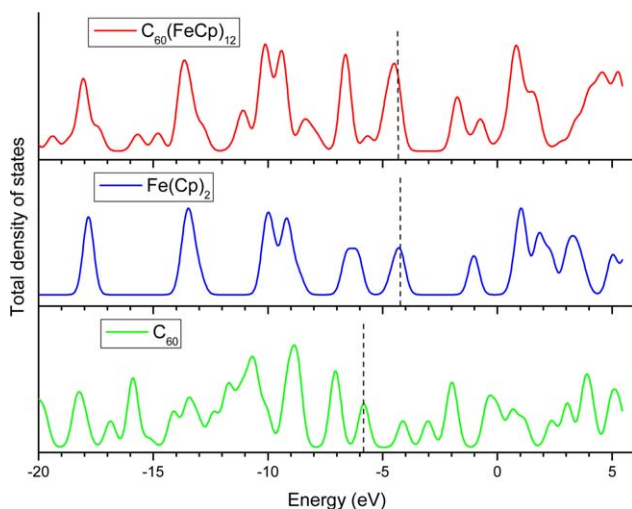


Figure 4. Calculated TDOS for a) $C_{60}(FeCp)_{12}$, b) $Fe(Cp)_2$, and c) C_{60} , HOMOs are marked by the vertical dashed line.

The calculated rotation barrier between the two configurations is 0.57 eV at the same theoretical level, which is almost 14 times as that of ferrocene from the eclipsed geometry (D_{5h}) to the staggered (D_{5d}) structure (0.04 eV).

The calculated HOMO–LUMO gap of C_{60} is 1.71 eV at TPSS/6-31G*/LanL2DZ level of theory, in good agreement with the experimental values (1.57 eV),^[70] which confirms the reliability of our method. The calculated HOMO–LUMO gap of $C_{60}(FeCp)_{12}$ is 2.53 eV, just between C_{60} (1.71 eV) and ferrocene (3.20 eV), indicating its high electronic stability. Moreover, as the HOMO–LUMO gap of $C_{60}(FeCp)_{12}$ is much larger than that of C_{60} , we could infer that the electronic structure of $C_{60}(FeCp)_{12}$ is different from C_{60} but trends to be similar as ferrocene.

Figure 2 compares the geometric parameters of $Fe(Cp)_2$, C_{60} , and $C_{60}(FeCp)_{12}$ molecules. It is well known that there are two kinds of C–C bonds with different bond length in C_{60} molecule—the one between the C_5 ring and C_6 ring is 1.46 Å and the other between two C_6 rings is 1.40 Å, which could be considered as the single and double bonds separately. However, in inner C_{60} cage of $C_{60}(FeCp)_{12}$, all the C–C bond length is uniform of 1.45 Å. Thus, the special long-short bonding system in C_{60} is broken when coordinating 12 (FeCp) ligands. Other chemical bonds in $C_{60}(FeCp)_{12}$ are also taken into consideration. The Cp ligand in $C_{60}(FeCp)_{12}$ has the same C–C bond length as ferrocene (1.44 Å). For the Fe–C bond, the bond length of Fe–Cp in $C_{60}(FeCp)_{12}$ is equal to that of $Fe(Cp)_2$ (2.04 Å), and the length of Fe– C_{60} bond is a little longer (2.09 Å).

By comparing the structure of $C_{60}(FeCp)_{12}$ with C_{60} and ferrocene, we found that although the hybrid compound $C_{60}(FeCp)_{12}$ keeps the similar icosahedral geometry structure as C_{60} , its electronic structure may change. The electronic delocalized π system of C_{60} is broken when coordinating the (FeCp) ligands. As the C_5 rings in $C_{60}(FeCp)_{12}$ have the similar bond length as Cp ligands in ferrocene (1.45 Å and 1.44 Å, separately), we suppose that the $C_{60}(FeCp)_{12}$ molecule could be viewed as the combination of 12 $Fe(Cp)_2$, each $Fe(Cp)_2$ unit has the similar electronic structure as ferrocene.

Chemical bonding analysis

To confirm our inference for the electronic structure of $C_{60}(FeCp)_{12}$, chemical bonding analysis is performed using AdNDP method. As a comparison, we first give the AdNDP chemical bondings of ferrocene. Figure 3a reveals that there are nine delocalized 15c-2e bonds in ferrocene, which is in accordance with our former study.^[71] These 15c-2e orbitals can be clearly viewed as super S , P_{xyz} and $D_{xy^2z^2xz^2-y^2z^2}$ orbitals from their orbital symmetry, which are formed by the delocalized π orbitals of two Cp ligands and the valence spd orbitals in Fe. As the whole $C_{60}(FeCp)_{12}$ compound is too large to do AdNDP analysis, we choose its tripolymer unit (H_3C_5FeCp)₃ for analyzing (one $C_{60}(FeCp)_{12}$ compound is

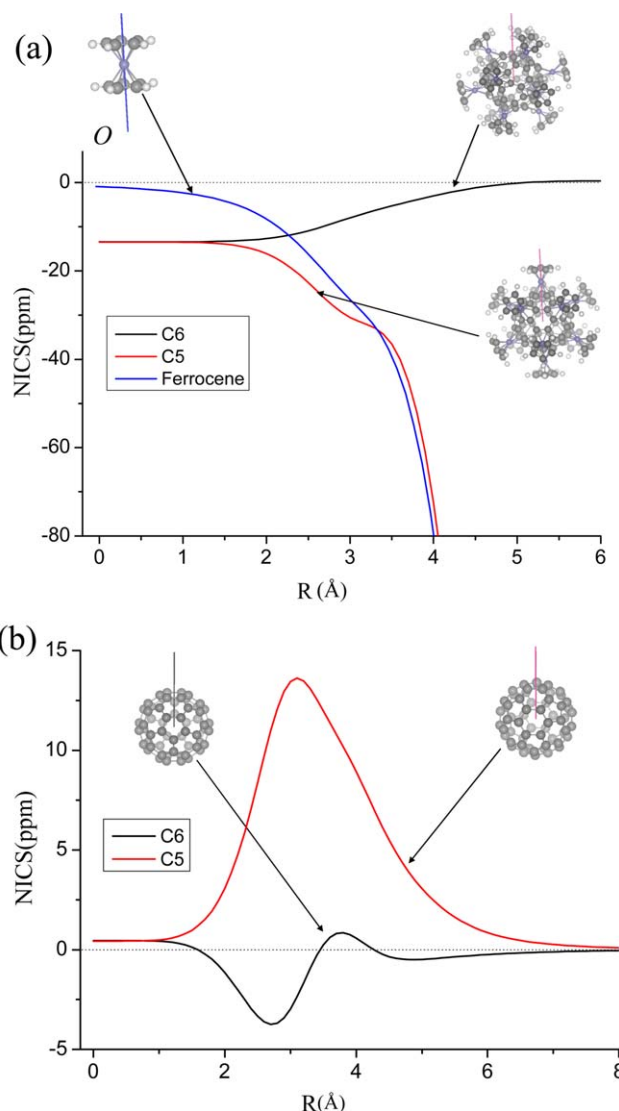


Figure 5. The NICS_{zz}-scan curves for a) $C_{60}(FeCp)_{12}$ (scanning along the center of C_5 ring (red) and C_6 ring (black) within the range of 0.0–6.0 Å above the geometric center of $C_{60}(FeCp)_{12}$, respectively) and $Fe(Cp)_2$ (scanning along the center of the Cp ligand (blue) within the range of 0.0–6.0 Å, the point 5.0 Å below the bottom Cp surface is setting as the zero point); b) C_{60} (scanning along the center of C_5 ring (red) and C_6 ring (black) within the range of 0.0–8.0 Å above the geometric center of C_{60} , respectively).

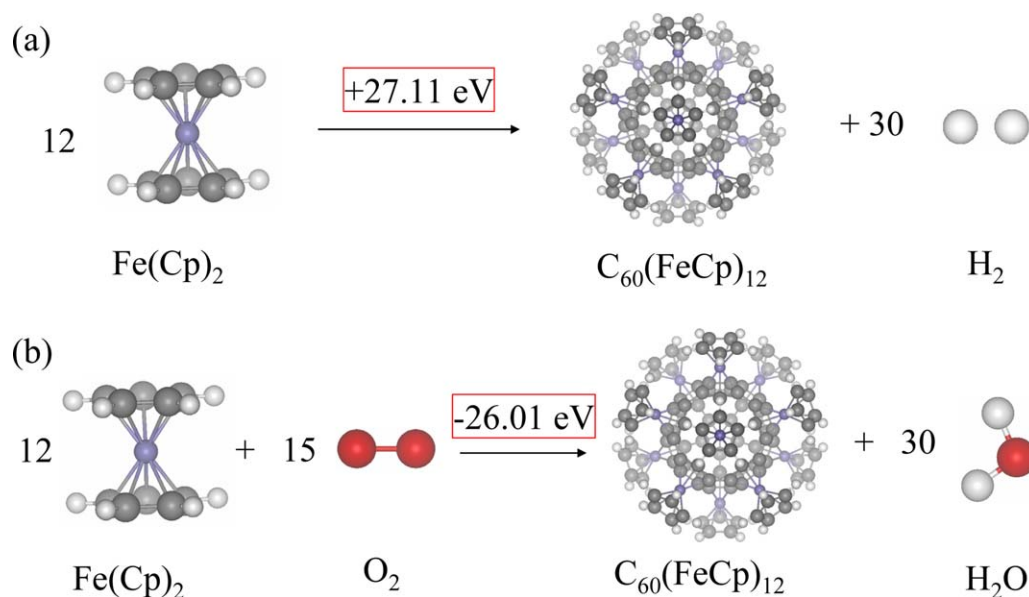


Figure 6. Formation process of $\text{C}_{60}(\text{FeCp})_{12}$ by a) direct dehydrogenization reaction and b) oxidation reaction, reaction energies (eV) at TPSS/6-31G*/LanL2DZ level are labeled.

consisted of four same tripolymer units). As shown in Figure 3b, we could identify that one ($\text{H}_3\text{C}_5\text{FeCp}$) unit of the tripolymer also has nine delocalized 15c-2e chemical bonds, which are formed by the interaction between the valence *spd* orbitals of Fe atom and the delocalized π orbitals of the Cp ligand and the C_5 unit in (H_3C_5)₃ face. These bonds could be viewed as the super *S*, *P*_{*xyz*}, and *D*_{*xyyzxzxz2-y2z2*} orbitals as Fe(Cp)_2 . Figure 3b also reveals that all the π orbitals of the C_5 units are involved in the *spd*- π interaction. So there is no delocalization between three ($\text{H}_3\text{C}_5\text{FeCp}$) units, and they connect each other by the C—C single bond to form the tripolymer and then, the whole $\text{C}_{60}(\text{FeCp})_{12}$ compound.

These AdNDP results indicate that the delocalized system of C_{60} cage in $\text{C}_{60}(\text{FeCp})_{12}$ compound has been changed after coordinating the (FeCp) ligands. From the electronic character, the $\text{C}_{60}(\text{FeCp})_{12}$ compound could be considered as the union of 12 Fe(Cp)_2 , which is in accordance with our inference. Furthermore, the total density of states (TDOS) for Fe(Cp)_2 , C_{60} , and $\text{C}_{60}(\text{FeCp})_{12}$ are calculated and plotted in Figure 4 as reference. The TDOS curve of $\text{C}_{60}(\text{FeCp})_{12}$ have the similar characters as Fe(Cp)_2 but is quite different from the TDOS of C_{60} , which confirms the AdNDP results.

Aromaticity

The AdNDP results of $\text{C}_{60}(\text{FeCp})_{12}$ indicate that the monomer unit of $\text{C}_{60}(\text{FeCp})_{12}$ has the similar electronic structure as Fe(Cp)_2 . To further validate this conclusion, we study the aromaticity for this compound. The nucleus independent chemical shift (NICS) is an easy and efficient criterion for aromaticity,^[72] in which the negative value means aromaticity and the positive value means antiaromaticity. We calculate the NICS values along the central *X*-axis of the C_5 ring and C_6 ring in $\text{C}_{60}(\text{FeCp})_{12}$ compound within the range of 0.0–6.0 Å, respectively (the zero point is setting at the geometry center of the

compound). The NICS_{zz}-scan curves are shown in Figure 5a, and the NICS curve along the central *X*-axis of Fe(Cp)_2 compound within the same range is also plotted as reference. To make their NICS results comparable, we choose the point 5.0 Å below the bottom Cp face as the zero point for NICS scanning of Fe(Cp)_2 , as the geometry center of $\text{C}_{60}(\text{FeCp})_{12}$ is also 5.0 Å below the inner C_5 ring surface.

NICS curve shows the negative value around the center of the $\text{C}_{60}(\text{FeCp})_{12}$ compound, which indicates its high aromaticity. But as the range increasing, the value along the center of the C_5 ring rises while it decays rapidly along center of the C_6 ring. In the face center of the C_6 ring, NICS value is approaching zero, indicating rarely aromaticity. So, we infer that C_6 ring itself is almost nonaromaticity and the negative NICS value at the central point of the compound is derived from the C_5 ring. Thus, we conclude that the π systems only delocalize inside the C_5 rings and there is no delocalization inside the C_6 rings of the $\text{C}_{60}(\text{FeCp})_{12}$, which is in accordance with the AdNDP results. Furthermore, when comparing with ferrocene, we found that the NICS curve shape of the C_5 ring is closely similar to that of Fe(Cp)_2 compound. And in the zero point, the NICS value of the C_5 ring is almost 12 times as that of ferrocene, which is another evidence that $\text{C}_{60}(\text{FeCp})_{12}$ complex could be view as the combination of 12 ferrocene molecules.

What is more, the NICS value of C_{60} is also calculated for comparison. The scanning range is from 0.0 to 8.0 Å (the zero point is setting at the geometry center of the compound) along the central *X*-axis of the C_5 ring and C_6 ring, respectively. The NICS scanning curves in Figure 5b are totally different from the NICS results of $\text{C}_{60}(\text{FeCp})_{12}$. As the C_{60} molecule has a delocalized π system with 60 electrons which do not follow the $2(N+1)^2$ rules of spherical aromaticity,^[73] the NICS value of its geometry center is positive. From the shape of these NICS curves, we could infer that π electrons of C_{60} are mainly localized on the short C—C bonds between two C_6 rings.

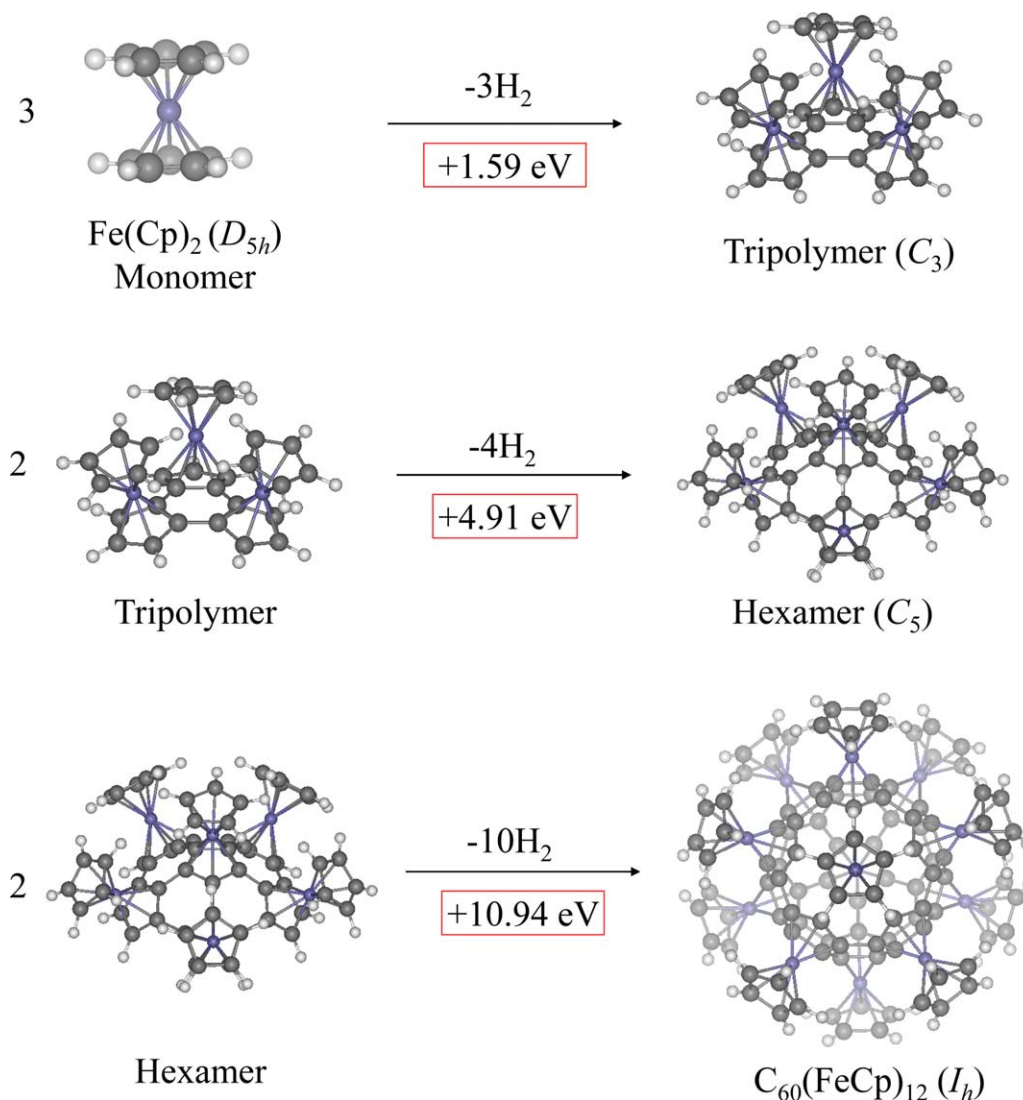


Figure 7. Stepwise formation process of $C_{60}(\text{FeCp})_{12}$, reaction energies (eV) at TPSS/6-31G*/LanL2DZ level are labeled.

So, we could reconfirm that the delocalized system of C_{60} cage has been changed after coordinating 12 (FeCp) ligands, and the character of aromaticity is a further evidence for the similarity between $C_{60}(\text{FeCp})_{12}$ and Fe(Cp)_2 in their electronic properties.

Predicted formation process

From all above, we found that the $C_{60}(\text{FeCp})_{12}$ molecule has the geometry structure as C_{60} and the electronic properties as ferrocene, which indicates that it would get variety of chemical properties and extensive application foreground. But so far, there is no experimental report on the synthesis process of this molecule. As the high delocalization energy of the 60-electronic delocalized π system in C_{60} , traditional synthetic method is difficult in adding 12 ligands in the C_{60} cage. But as the similarity of electronic characters between $C_{60}(\text{FeCp})_{12}$ and ferrocene, we suppose that $C_{60}(\text{FeCp})_{12}$ could be synthesized from ferrocene molecules. So in the last section, we theoretically discuss this unconventional formation process of the

$C_{60}(\text{FeCp})_{12}$ compound, and hope it would give some references for its experimental synthesis.

Figure 6 shows the synthesis routes of $C_{60}(\text{FeCp})_{12}$ from 12 Fe(Cp)_2 molecules. The route in Figure 6a is a direct dehydrogenation reaction with the reaction energy of +27.11 eV. Figure 6b shows the oxidation reaction process with the oxygen as the oxidant, and its reaction energy is -26.01 eV. These two processes are endothermic and exothermic reactions, respectively, and their reaction energies are in the common range, which indicates their thermodynamic possibility. But considering the chemical reaction kinetics, the multicomponent reaction with 12 reactant molecules is hard to happen. So, we design the stepwise formation process in Figure 7, in which the whole process is divided into three steps. In the first step, three monomer Fe(Cp)_2 molecules form the tripolymer unit. In the second step, two tripolymers form a hexamer. Finally, two hexamers form the $C_{60}(\text{FeCp})_{12}$ molecule. The reaction energies for the three steps are +1.59 eV, +4.91 eV, and +10.94 eV, respectively. The tripolymer (C_3) and hexamer (C_5) units in this process could be viewed as the eclipsed

configurations with a little distortion. They are the local minimum structures which have the lower energy than the perfect eclipsed configurations due to the calculation.

However, as there are two symmetrical Cp ligands in the Fe(Cp)₂ compound, the orientation of the reactants in these reactions is hard to control. So, we consider that the asymmetrical CCl₃FeCH₃ molecule (five H atoms in one Cp ligand are replaced by Cl atoms in Fe(Cp)₂) could be used instead of Fe(Cp)₂ to ensure the orientation of the reactants during the formation process. As the experimental synthesis process is usually complicated, our theoretical discussion just provides an unconventional thought as reference. Great efforts of researchers are still needed for studying the practical synthetic route of C₆₀(FeCp)₁₂ in the future.

Conclusions

In this article, we build the structure of I_h-C₆₀(FeCp)₁₂ compound and theoretically investigate its geometry and electronic properties using DFT method. After optimizing, C₆₀(FeCp)₁₂ maintains its I_h symmetry with a large HOMO–LUMO gap, and its inner face keeps the C₆₀ cage structure. But the AdNDP chemical bondings, aromaticity and the TDOS of C₆₀(FeCp)₁₂ are proved to be similar as Fe(Cp)₂, which reveals that the delocalized π system of C₆₀ has been broken when coordinating 12 (FeCp) ligands. This result indicates that the C₆₀(FeCp)₁₂ compound has the geometry structure as C₆₀ and electronic property as ferrocene, so it would inherit special characters from both C₆₀ and ferrocene. To provide some references for the experimental synthesis of the C₆₀(FeCp)₁₂ compound, its possible formation process is predicted theoretically in the last part of this article. The unconventional synthetic routes of C₆₀(FeCp)₁₂ from 12 Fe(Cp)₂ molecules are proposed and their reaction energies are calculated.

When fullerene meets ferrocene, it would bring out various possibilities in chemistry. We hope that our study would provide a perfect hybrid compound with wild potential applications in the future chemical field.

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Keywords: fullerene · ferrocene · π-complexes · aromaticity

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