The effect of C$_{60}$ on the optical absorption properties of HPPH photosensitizer

C H Zhou$^{1,2}$, Z H Sun$^1$, J C Zhang$^1$ and G Fan$^1$

$^1$Department of Chemistry and Chemical Engineering, Xianyang Normal University, Xiangyang 712000, China
E-mail: xbdxzch@126.com

Abstract. The optical absorption properties of the clinical photosensitizer (HPPH) and HPPH-C$_{60}$ dyads (HPPH-C$_{60}$ (1), HPPH-C$_{60}$ (2) and HPPH-C$_{60}$ (3)) have been calculated by density functional theory (DFT) and time dependent density functional theory (TD-DFT). Based on the optimized geometrical structures of three HPPH-C$_{60}$ dyads, their binding energies, the charges populations and the excited energies are calculated specifically. The results show that the different binding sites between C$_{60}$ and HPPH induce the different binding energy. The maximum binding energy and the significant charge transfer occur at C$_{60}$ and nitrogen atoms of HPPH in HPPH-C$_{60}$(1). At the same time, the excited energies of three HPPH-C$_{60}$ dyads are smaller than that of HPPH. The maximum absorption peak of the HPPH-C$_{60}$(1) reaches near infrared 961.69nm.

1. Introduction

In recent years, it is attracted great attention that the photosensitizer applying to photodynamic therapy. As the third generational photosensitizer, HPPH has remarkable curative effect in clinical treatment [1-3]. So it has been widely applying to cure skin cancer maculopathy adjuvant therapy. However, HPPH still belongs to porphyrin drugs, and porphyrin rings are modified by carbonyl groups and hydroxyl groups, it can reduce molecular symmetry and conjugation. The investigation shows that HPPH has hardly enough triplet state energy, which induces low singlet oxygen yields. So a low dosage of HPPH has slight therapeutic effect, it needs repeated treatment [4-5]. But too much oxygen radical will injure cytomembrane, which has great toxic and side effect. So that it is very urgent to improve the effect of treatment.

Fullerenes are a class promising bioactive materials [6-7], which can be apply to the anticancer and photodynamic therapy. For example, during the beginning of the twentieth century, the antitumor effect of C$_{60}$-PEG compound had been reported by Tabata[8]. It is found that C$_{60}$-PEG can stay at cancer cell for longer time and have better antitumor effect than clinical photosensitizer photofrin. In 2007, Witte reported that fullerene can interaction with cytochrome C. That is, the stable compound can be formed by fullerene photosensitizer and DNA, which can depress the reproduction of cancer cells when it injects into biological body [9]. In 2015, Francis D'Souza designed one kind of fullerene photosensitizer containing pyrrole and porphyrin groups, winch has great triplet efficiency and powerful infrared absorption ability [10]. He predicted that those fullerene derivatives can be as potential photosensitizer. At the same time, Bang ping et al. synthesized water-soluble carbon nano-materials and phthalocyanin compounds that can be used to photodynamic therapy [11]. In 2015, it is
proved that single-walled carbons nanotubes will effective promote the yields of singlet oxygen and enhance photodynamic effects [12].

The above extensive researches showed that complexed carbon nanomaterials such as fullerene combined with porphyrin, will enhance singlet oxygen yields of prophyrin photosensitizers and enlarged absorption peak of photosensitizers to vis-infrared regions. So it is so important to develop fullerene-porphyrin photosensitizer for promoting photodynamic effects. However, we still need further study the intrinsic properties of fullerene-porphyrin complexes. Such as, the combined sites, the modes of interaction and the change of absorption spectra for fullerene and porphyrin. So the structure and the optical absorption properties of the HPPH are calculated by DFT/TD-DFT in this paper. Based on above calculated results, according to possible interaction site of C$_{60}$ and HPPH, it can get three kinds of stable composites, HPPH-C$_{60}$(1), HPPH-C$_{60}$(2) and HPPH-C$_{60}$(3). The binding energy, charge population and excited energy of three kinds of composites are also calculated using DFT/TD-DFT. The intrinsic reason for C$_{60}$ promoting HPPH optical absorption properties is discussed.

2. Computing method

Based on the density functional theory (DFT) with the M06-2X[13,14] exchange-correlations, geometry structures and vibration frequency of four complexes are calculated in this work. All examined complexes are no symmetry constraints. Using the adiabatic approximation of time dependent density functional theory TD-DFT/M06-2X/6-31+G(d, p), their excited energies and oscillator strengths are computed. For ground state structure optimizations, it is used that the split valence plus polarization basis sets 6-31+G(d, p) is for nonmetal (H, C, N, S, O) atoms. The counterpoise correction was used to correct for the basis set superposition error (BSSE) at the same level of theory as used for the geometrical optimizations [15-17]. BSSE is calculated with the counterpoise procedure method advance by Boys and Bernardi[16]. The corrected interaction energy (ΔE) shown that

\[ \Delta E = E(\text{HPPH-C}_{60}) - E(\text{HPPH}) - E(\text{C}_{60}) \]

In this formula, E(\text{HPPH-C}_{60}) is the energy of composites(\text{HPPH-C}_{60}(1), \text{HPPH-C}_{60}(2) and \text{HPPH-C}_{60}(3)). E\text{HPPH (C}_{60}) is the energy of HPPH based on all the atoms are set as puppet atoms with virtual orbital in C$_{60}$. E\text{C}_{60}(\text{HPPH}) is the energy of C$_{60}$ based on all the atoms be set as puppet atoms with virtual orbital in HPPH. Based on calculated results from Gaussian09, the optical absorption spectra are simulated by SWizard program[18], and the peak half-width is set in 0.209eV(1685.83cm$^{-1}$).

3. Results and discussion

3.1. The Ground-state structure of HPPH-C$_{60}$ composites

Based on M06-2X/6-31+G(d, p), three structures of HPPH-C$_{60}$ composites are completely optimized. The Figure 1 shows stable configurations of three composites without imaginary frequency. The weak interactions between C$_{60}$ and HPPH are found in Figure 1. In composites HPPH-C$_{60}$(1), the weak interactions are from carbon atoms of C$_{60}$ with nitrogen atoms of porphyrin ring, their shortest distance is 2.52Å. In another two composites, the weak interactions are between C$_{60}$ and HPPH are 1.94 Å and 2.41 Å, respectively.
Figure 1. The structures of HPPH (a), HPPH-C₆₀(1) (b), HPPH-C₆₀(2) (c) and HPPH-C₆₀(3) (d).

It is found that the C=N and C=C bonds are elongated in three composites, comparing with those in HPPH. The biggest deviation is less than 3%, it means that the weak interaction slightly influence on geometrical structure of porpyrin ring. Based on BSSE correction, the binding energies of three composites (HPPH-C₆₀(1), HPPH-C₆₀(2) and HPPH-C₆₀(3)) are computed. Their binding energies are 0.4107eV, 0.2824eV and 0.3269eV, respectively. The computational formula of binding energy is as follow: E_{binding} = \sum |\Delta E| = E(C₆₀-HPPH) - E(C₆₀) - E(HPPH). From binding energies, it can find that the composites HPPH-C₆₀(1) has the biggest binding energy, the composites HPPH-C₆₀(2) has the least energy. So C₆₀ trends to interact with porpyrin ring in HPPH. That is, the C₆₀ can receive the charges from nitrogen atoms of porpyrin ring, and it is similar to many reports [18-22]. So the charge populations of three composites and HPPH are analyzed by natural bond orbital (NBO) theory. As Table 1 shown that the charge of N(1) is -0.2081e in HPPH, in three composites, the charge of N(1) is reduced, they are -0.2067e, -0.2065e, and -0.2067e, respectively. It means that negative charges of nitrogen atoms are almost equal in three compounds. The charges of oxygen atoms in HPPH are affected by carbon atoms of C₆₀. For example, in HPPH-C₆₀(3), carbon atoms of C₆₀ interact with the O(23) and O(24) of HPPH, and the charges of O(23) and O(24) is lower than in HPPH molecule. So from binding energies and charge populations of three composites, it can see that the C₆₀ hardly influence geometrical structure of HPPH, and the charges transfer is from HPPH to C₆₀ in all composites. Among three composites, the binding energy of HPPH-C₆₀(1) is the biggest, the charge transfer is also the most obvious for HPPH-C₆₀(1).

Table 1. The NBO charge populations of partial atoms for HPPH and three composites.

| Charge /e | HPPH   | HPPH-C₆₀(1) | HPPH-C₆₀(2) | HPPH-C₆₀(3) |
|-----------|--------|------------|------------|------------|
| N(1)      | -0.2081| -0.2067    | -0.2065    | -0.2067    |
| N(2)      | -0.0243| -0.0269    | -0.0242    | -0.0245    |
| N(3)      | -0.0476| -0.0498    | -0.0476    | -0.0472    |
| N(4)      | -0.2033| -0.2002    | -0.2032    | -0.2032    |
| O(17)     | -0.1067| -0.1059    | -0.1051    | -0.1074    |
| O(18)     | -0.2550| -0.2533    | -0.2545    | -0.2548    |
| O(19)     | -0.1171| -0.1188    | -0.1188    | -0.1192    |
| O(20)     | -0.1595| -0.1578    | -0.1599    | -0.1627    |
| O(21)     | -0.2196| -0.2202    | -0.2306    | -0.2238    |
| O(22)     | -0.2661| -0.2698    | -0.2691    | -0.2699    |
| O(23)     | -0.1055| -0.1052    | -0.1055    | -0.0952    |
| O(24)     | -0.2559| -0.2562    | -0.2556    | -0.2530    |
3.2. The Absorption spectra simulation of HPPH and three composites

Absorption spectra of photosensitizers is an important character, so absorption spectra of three composites (HPPH-C₆₀(1), HPPH-C₆₀(2) and HPPH-C₆₀(3)) and HPPH are calculated and discussed in details.

![Figure 2. The absorption spectra of HPPH and its three composites.](image)

Based on the calculated excited energies, absorption spectra of HPPH and three composites (HPPH-C₆₀(1), HPPH-C₆₀(2) and HPPH-C₆₀(3) are simulated in Figure 2. the first excited energy of HPPH is the biggest, the excited energies of HPPH-C₆₀(2) and HPPH-C₆₀(3) are almost similar. The longest absorption bands are 759.74nm and 765.40nm, and the extinction coefficient reach 10⁵ in HPPH-C₆₀(2) and HPPH-C₆₀(3), so their longest absorption bands are the longer than that of HPPH. For the longest absorption wavelength of HPPH, the calculated value is 658.09nm, which is very close with the experimental value 660nm[23]. The first excited energy of HPPH-C₆₀(1) is the smallest among three composites, so the longest absorption band of HPPH-C₆₀(1) reaches 946.96nm. It is proved that C₆₀ can extend the longest absorption band of HPPH. That is, C₆₀ can improve the light injection efficiency of HPPH photosensitizer in photodynamic therapy.

Table 2. The frontier orbital’s energies of HPPH and three compounds.

|          | HPPH  | HPPH-C₆₀(1) | HPPH-C₆₀(2) | HPPH-C₆₀(3) |
|----------|-------|------------|------------|------------|
| HOMO     | -4.475| -4.445     | -4.522     | -4.593     |
| LUMO     | -3.091| -3.796     | -3.827     | -3.821     |
| ΔE_L-H   | 1.384 | 0.649      | 0.695      | 0.772      |

![Figure 3. The frontier orbital constitutional diagram of HPPH-C₆₀(1).](image)

To reveal the effects of electronic structures on absorption bands of composites, their frontier orbital energies and the atomic orbital components of HPPH-C₆₀(1) are calculated and analyzed. From Table 2, it can be seen that their highest occupied orbital energies are almost similar in three
composites, but their lowest unoccupied orbital energies are reduce obviously, comparing with those orbitals in HPPH. It causes the energy gaps between the lowest unoccupied orbital and the highest occupied orbital of three composites are smaller than energy gap between the lowest unoccupied orbital and the highest occupied orbital of the HPPH. From Figure 3 shown, for HPPH-C_{60} (1), the highest occupied molecular orbital is still from porphyrin ring, and the lowest unoccupied molecular orbital is from \( \pi \) orbital of fullerene. The energy gap of HPPH-C_{60} (1) is the smallest among three composites. The frontier orbital populations of HPPH-C_{60}(2) and HPPH-C_{60}(3) are similar to HPPH-C_{60}(1), but their energy gaps are lower than that of HPPH-C_{60}(1). It is note that the energy gap of frontier orbitals (HOMO and LUMO) are not equally to the first excited energy, because the electronic excitation also considers the orbital symmetry besides the orbital energy.

4. Conclusion
In conclusion, based on optimized structures of HPPH photosensitizer and its three composites (HPPH-C_{60}(1), HPPH-C_{60}(2) and HPPH-C_{60}(3), their binding energies, charge populations and excited energies have been calculated by density functional theory. The calculated results show that the weak interactions between the donating electron atoms of HPPH and C_{60} resulting into three stable composites. Among three composites, HPPH-C_{60}(1) has the greatest binding energy, in which C_{60} interacts with nitrogen atoms of porphyrin ring and the obvious charge transfer can be found from nitrogen of HPPH to C_{60}. From the calculated excited energies, it can find that three composites have less excited energies than HPPH do, simulated absorption bands of three composites also are longer than that of HPPH. The above results due to the unoccupied orbitals of C_{60} are lower than the unoccupied orbitals of HPPH, as a result, occupied electrons can easily excited to unoccupied orbitals in composites. Especially, the absorption wavelength of HPPH-C_{60}(1) reaches 946.9nm, which belongs to infrared region of the solar light.

Acknowledgement
This work was supported by the Specialized Research Fund of Xian yang Normal University (No. 14XSYK013, 15XSYK040), the 56th China Postdoctoral Science Foundation (No. 2014M560758), and National Undergraduate Training Programs for Innovation and Entrepreneurship(NO. 201610722011).

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