DFT-TDDFT Computational Study of Three Different Chlorophyllous as Dye sensitized solar cells (DSSCs)

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Abstract

Dye sensitized solar cells (DSSCs) are currently attracting widespread academic and commercial interest for the conversion of sunlight into electricity because of their low cost and high DSSCs are similar to natural photosynthesis in the initial processes involving in light-harvesting and charge separation. To gain a better understanding of the role of the sensitizer, particularly of its electronic structure and excited-state properties in the efficiency of dye-sensitized solar cell devices, we have carried out Density Functional Theory (DFT) and Time Dependent DFT (TDDFT) calculations in solution of the geometry, electronic structure and optical absorption spectra of a Chl a derivative and its Mg-Phe a and Zn-Phe a -derived sensitizers. Calculations have been performed using the B3LYP exchange correlations functional, as implemented in the Gaussian03 program package. The geometries of were first optimized in vacuum using density functional 6-311G(d) method. Solvation effects were included by means of the Conductor-like polarizable continuum model (C-PCM) in the dichloromethane solvent. There is good agreement between the experimental and the TDDFT calculated absorption spectra of three Different Chlorophyllous sensitizers. Natural bond orbital (NBO) analysis was also conducted on optimized geometries with the NBO program included in the Gaussian program package. From the orbital analysis and the orbital spatial orientation of HOMO and LUMO for Phe a, Mg-Phe a and Zn-Phe a -derived sensitizers, the result shows that Phe a seems to provide higher photo-to-electric conversion efficiencies.

1. Introduction

Natural photosynthetic systems have evolved over billions of years, and they can therefore provide hints regarding some possible strategies for improving the performance of organic photovoltaic systems such as dye-sensitized solar cells (DSSCs)[1]. Chlorophylls (Chls) play a fundamental role in photosynthesis. They are the molecular species that are responsible for both light energy capture and its conversion into an electrochemical gradient. In photosynthetic oxygen evolving organisms, such as plants and cyanobacteria, two photosystems called photosystem I and photosystem II (PS I and PS II) capture and convert solar energy independently (but cooperatively). Several types of chlorophyll (Chl) are presented the photosynthetic systems. In both PS I and PS II, the molecular species at the heart of all of the solar capture and conversion processes is chlorophyll-a (Chl-a) [2].

In light-harvesting antenna complexes (LHCs), Chl b or Chl c plays the role of an accessory pigment by transferring its excitation energy to Chl a, which is present in both groups of plants. Both delocalized energy- and electron-transfer in some mutant of higher plants can sometimes be mediated by Chl a without Chl b, and this means that efficient non-irradiative energy transfer might not be necessarily dependent on multi-pigments structure[3].

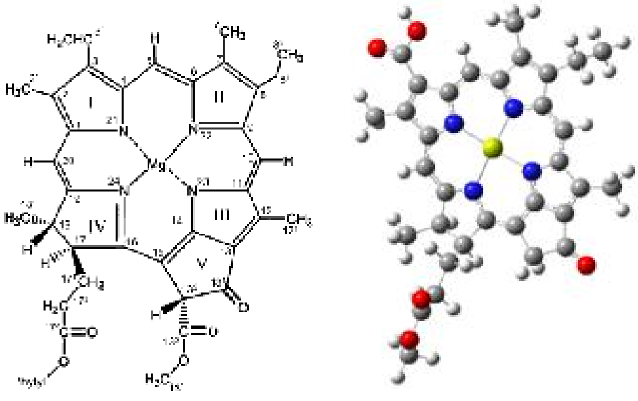


Fig.1. Molecular structure and IUPAC numbering scheme of Chl a.

Chl a is the major pigment found in all oxygenic photosynthetic organisms. The molecular structure of Chl-a is shown in Fig. 1. It contains three carbonyl (C=O) groups at the 13^1, 13^3 and 17^3 positions[2]. As it can be seen, Chls is containing a macro cycle of porphyrin. In recent years different porphyrins and their metal derivatives, have been used as photo-sensitizers for polycrystalline TiO_2 in order to enhance the visible light-sensitivity of the TiO_2 matrix and thereby increases its photocatalytic activity [4-9]. It was shown that the central coordinated metal in porphyrins plays a critical role in the photocatalytic processes of the porphyrin–TiO_2 system [10].

Since lots of sensitizers with carboxyl acid group as anchoring group to the surface of the TiO_2 nanoparticles have been proved efficient to inject excited electron to the conductive band of TiO_2, in which case the carboxyl acid group is a donor and the TiO_2 is an acceptor, those sensitizer candidates which can transport electron from the other part of the sensitizer to the carboxyl acid group are thus rationally considered promising to be able to inject excited electrons to the conduction band of the TiO_2 particles. A sensitizer molecule with the carboxyl acid-containing group being considered as acceptor can reflect the electron transfer mechanism approximately, although a much more complicated model combining the sensitizer and the TiO_2 particle together is more exact[11].

In this study, we have carried out Density Functional Theory (DFT) and Time Dependent DFT (TDDFT) calculations in solution of the geometry, electronic structure and optical absorption spectra of a Chl a derivative (methyl 3-devinyl-3-carboxypyropheophorbide a; Phe a) and its Mg-Phe a and Zn-Phe a -derived sensitizers. Calculations have been performed using the B3LYP exchange correlations functional, as implemented in the Gaussian03 program package. The geometries of were first optimized in vacuum using density functional 6-311G(d) method. Solvation effects were included by means of the Conductor-like polarizable continuum model (C-PCM) in the dichloromethane solvent. Natural bond orbital (NBO) analysis was also conducted on optimized geometries with the NBO program included in the Gaussian program package.

2. Results and discussion

2.1. Molecular orbital of the Phe a, Mg-Phe a and Zn-Phe a

The charge transfer orientation is associated with the distribution of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the sensitizer.

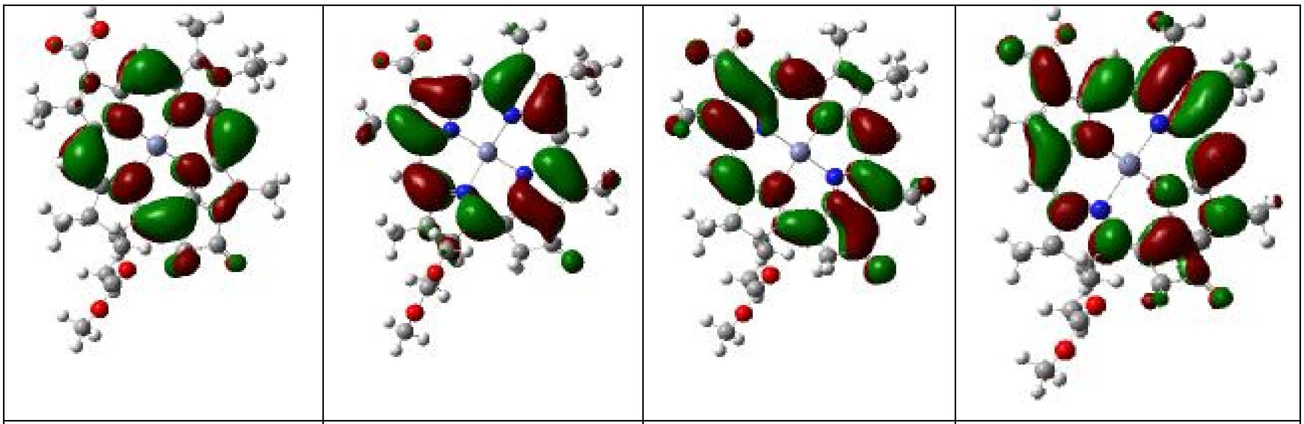
Table 1. Orbital energy levels of Zn-Phe a (eV)

Molecule	**HOMO**	**Δ HOMO-LUMO**	**LUMO**
Phe a	-5.377	2.398	-2.978
Mg- Phe a	-5.256	2.324	-2.932
Zn- Phe a	-5.262	2.348	-2.914

The data of HOMO, LUMO and HOMO–LUMO gaps are given in Table 1. The HOMO and LUMO for Phe a are located at -5.377 and -2.978 eV, respectively. Similarly, the HOMO and LUMO of the other molecules are lower than those of Phe a. The energy gap between the HOMO and the LUMO is 2.398 eV for Phe a. The energy gaps of the other molecules are all smaller than that of Phe a. The order of the energy gaps is Zn- Phe a (2.324eV) > Mg-Phe a (2.348 eV) > Phe a. the smaller HOMO–LUMO gap indicates the higher photo-to-electric conversion efficiency. This trend can be explained as follows. Let us suppose that the HOMO of the sensitizer is lower enough than the redox potential of the electrolyte and the LUMO is higher enough than the conduction band of the TiO_2 particle, which indicates the open circuit voltage V_{oc} of the solar cell will not be influenced by the HOMO, LUMO variations. With the HOMO–LUMO gap decrease, more photons at the longer-wavelength side would be absorbed to excite the electrons into the unoccupied molecular orbital, which increases the short circuit current density J_{sc} and further the conversion efficiency η of the solar cell[11].

2.2. NBO analysis

Figure 2 Show the Molecular orbital spatial distribution for Zn-Phe a.



HOMO-1 HOMO LUMO LUMO+1

Fig. 2. Molecular orbital spatial distribution for Zn-Phe a.

2.3. Electronic absorption spectra of the Phe a, Mg-Phe a and Zn-Phe a

The calculated wavelengthes, oscillator strengthes and transition energies for the most relevant transitions of the electronic absorption bands of Phe a, Mg-Phe a and Zn-Phe a in the solvent were obtained through TDDFT calculations. The simulated electronic spectra of these molecules are shown in Fig. 3.

The Chls show a series of bands between 350 and 650 nm due to π-π* absorptions of the conjugated macrocycle. The Soret-bands of the Phe a have higher molar extinction coefficients than that of Mg- and Zn-Phe a. This indicates that these Phe a can absorb more light at the shorter-wavelength side, but Q-bands of Mg-Phe a have higher molar extinction coefficients than that of Phe a and Zn-Phe, that can absorb more light at the longer-wavelength side which is good to further increase the photo-to-electric conversion efficiency of corresponding solar cells.

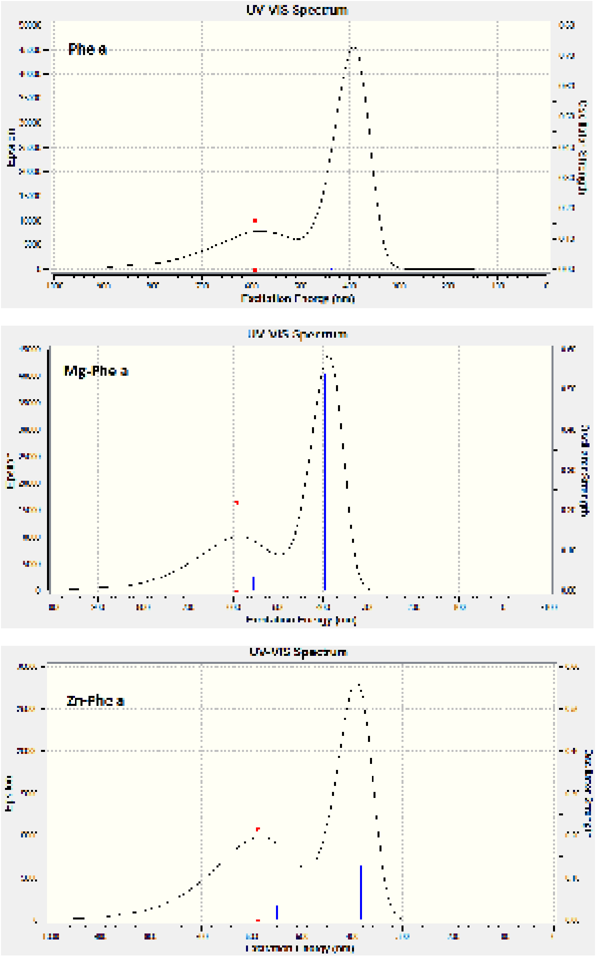


Fig. 3. simulated electronic spectra of Phe a, Mg-Phe a and Zn-Phe a

3. Conclusion

The electronic properties of Phe a, Mg-Phe a and Zn-Phe a have been investigated by B3LYP/6-311G(d) calculations to screen appropriate photo-to-electric conversion efficiencies. The electronic and spectroscopic properties of Phe a, Mg-Phe a and Zn-Phe a have been investigated by means of DFT/TDDFT calculations. There is good agreement between the experimental and the TDDFT calculated absorption spectra of three Different Chlorophyllous sensitizers.

When the sensitizer absorb light energy, it injects electron into the conduction band of the semiconductor. From the orbital analysis and the orbital spatial orientation of HOMO and LUMO for Phe a, Mg-Phe a and Zn-Phe a, the result shows that Phe a seems to provide higher photo-to-electric conversion efficiencies.

4. Methodology

The GAUSSIAN 03W package was used to perform geometry optimizations and time-dependent calculations (B3LYP/6-311G(d)) for Phe a, Mg-Phe a and Zn-Phe a. Percentage compositions of molecular orbitals were calculated using the NBO program.

The geometries of Phe a, Mg-Phe a and Zn-Phe a were first optimized in vacuum using density functional B3LYP/6-311G(d) method. None of the frequency calculations generated imaginary frequencies, indicating that the optimized geometries were true energy minima. The molecular orbital energy levels were compared for screening of the sensitizer candidates for DSSCs.

The electronic absorption spectra of the Phe a, Mg-Phe a and Zn-Phe a were calculated using the time-dependent density functional theory (TDDFT) method in the solvent. All the calculations were performed using the Gaussian03 program.

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