



# Theoretical investigation of self-assembled donor–acceptor phthalocyanine complexes and their application in dye-sensitized solar cells



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## ABSTRACT

A theoretical investigation of self-assembled donor–acceptor dyads (**ZnPca**, **ZnPcb** and **ZnPcc**) formed by axial coordination of zinc phthalocyanines appended with 4-carboxyl pyridine has been conducted with the density functional theory (DFT) method and time-dependent DFT (TD-DFT) calculations. A comparison between the molecular structures, atomic charges, molecular orbitals, UV–vis spectra and infrared (IR) spectra has been studied. Further, as sensitizers for the TiO<sub>2</sub>-based dye-sensitized solar cells, the photovoltaic performances have been investigated. The **ZnPcc**-sensitized solar cell exhibits a higher conversion efficiency than the **ZnPcb** and **ZnPca**-sensitized ones under AM 1.5 G solar irradiation, while the **ZnPca**-sensitized cell performs the poorest due to the lack of peripheral substituents (*n*-butyoxyl groups) which can be confirmed by the result of the theoretical research. It shows that the directionality of charge transfer in the self-assembled donor–acceptor dyads is important and benefit for the efficiency of the DSSC.

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## 1. Introduction

Studies on donor–acceptor dyads capable of undergoing light-induced electron or energy transfer are of current interest to mimic the primary events of the photosynthetic reaction center and also to develop molecular electronic devices [1–8]. Moreover, a large number of innovative researches are emerging, and remarkable achievements have been obtained. Toward constructing such dyads, porphyrins and phthalocyanines have been widely used as a energy/electron donor/acceptor due to their close resemblance to the photosynthetic pigment, chlorophyll, and the established synthetic methodologies [9,10]. Benzoquinone, methyl viologen, fullerene and perylene imides are particularly appealing as electron acceptors [11–15]. Self-assembly via metal–ligand axial coordination is one of the successful approaches developed to study photoinduced electron transfer in donor–acceptor dyads [16–19]. Spectroscopic, redox, and photochemical behavior of self-assembled donor–acceptor dyads formed by axial coordination of tetraphenylporphyrins and fulleropyrrolidine bearing either pyridine or imidazole coordinating ligands were investigated [20,21].

Majima and coworkers reported that the charge transfer of porphyrins and phthalocyanines to the axial ligand, pyromellitic imide, which acts as acceptors [22]. Singlet-singlet energy transfer in self-assembled via axial coordination of imidazole-appended free-base tetraphenylporphyrin, H<sub>2</sub>Plm, to either zinc phthalocyanine, ZnPc, or zinc naphthalocyanine, ZnNc, dyads was investigated in noncoordinating solvents [23]. Although there are a lot of reports on the charge transfer of self-assembled donor–acceptor dyads, there are few reports about the application of the dyads in dye-sensitized solar cells (DSSCs).

Phthalocyanines are well known chromophores for their intense absorption in the UV/blue (Soret band) and the red/near IR (Q band) spectral regions, as well as for their excellent electrochemical, photochemical and thermal stability. Furthermore, proper choice of substituents at the periphery of the macrocycle or metal coordination not only can adjust the photoelectrochemical properties, but also can effectively inhibit the aggregation and improve the solubility of phthalocyanines. In the above self-assembled donor–acceptor dyads, zinc porphyrins/phthalocyanines exist as electron donors with axial ligand containing carboxyl groups, phosphonic acid groups or sulfonic acid groups which can be coupled with TiO<sub>2</sub> semiconductor as electron acceptors. Electrons transfer from zinc porphyrin/phthalocyanine to the electron acceptor, and then inject into TiO<sub>2</sub> conduction band from the carboxyl group, phosphonic

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acid group or sulfonic acid group in the electron acceptor. It is possible to achieve directional charge transfer to the conduction band of TiO<sub>2</sub> semiconductor. Therefore, it is probable to realize the application of the dyads in DSSC.

In the present study, self-assembled donor–acceptor phthalocyanine complexes **ZnPca**, **ZnPcb** and **ZnPcc** were formed by axial coordination of symmetrical ZnPc,  $\beta$ -ZnPc(OBu)<sub>4</sub> and  $\alpha$ -ZnPc(OBu)<sub>4</sub> appended with 4-carboxyl pyridine, respectively, and a theoretical study for the molecular structures, atomic charges, molecular orbital energy gaps, molecular orbital spatial distribution, UV–vis absorption spectra, as well as infrared (IR) spectra of the self-assembled donor–acceptor dyads based on density functional theory was conducted. In addition to the theoretical investigations, to further confirm the directional charge transfer in the dyads, **ZnPca**, **ZnPcb** and **ZnPcc** have been used as dye sensitizers to sensitize TiO<sub>2</sub>, and their performances in DSSC have been explored. Both experimental and theoretical studies have demonstrated the directional charge transfer in the dyads.

## 2. Experiments

### 2.1. Chemicals and Instrumentation

Zinc phthalocyanine (ZnPc), 1,8,15,22-tetrakis (*n*-butyoxyl) zinc phthalocyanine ( $\alpha$ -ZnPc(OBu)<sub>4</sub>) and 2,9,16,23-tetrakis (*n*-butyoxyl) zinc phthalocyanine ( $\beta$ -ZnPc(OBu)<sub>4</sub>) were synthesized according to reported procedures [24,25]. All of the other reagents and solvents were used as received. The dye-sensitized solar cells were fabricated and tested according to our previous study [26,27].

### 2.2. Computational details

In this paper, the density functional B3LYP (Becke–Lee–Young–Parr composite of exchange–correlation functional) method was used to calculate the structures and vibration properties with LANL2DZ basis set [28–31]. In all work, the LANL2DZ basis set was used for the central metal atoms, and the 6-31G(d) basis set was used for the other atoms. Charge distribution was carried out using a full natural bond orbital analysis (NBO) population method based on the minimized structure with NBO 3.1 in the Gaussian 03 program. The UV–vis absorption spectra were calculated using the TD-DFT method based on the optimized structures with forty singlet-excited states. Gaussian bands with half-bandwidths of 500 cm<sup>-1</sup> were used to simulate the UV–vis absorption spectra. For all case, B3LYP method and LANL2DZ basis set were used. All calculations were carried out using the Gaussian 03 program in the IBM P690 system in Shandong Province High Performance Computing Centre.

## 3. Results and discussion

### 3.1. Molecular structures

The primal input structure of **ZnPca** was obtained by putting Zn<sup>2+</sup> ions into the central cavity of the phthalocyanine dianion, and one 4-carboxyl pyridine molecule was further introduced at the axial position of ZnPc; *n*-butyoxyl groups were added at the non-peripheral  $\beta$  position of the optimized structure of ZnPc to construct molecule **ZnPcb**; *n*-butyoxyl groups were added at the non-peripheral  $\alpha$  position of the optimized structure of ZnPc to construct molecule **ZnPcc**.

The structure and atom labeling of **ZnPca**, **ZnPcb** and **ZnPcc** are shown in Fig. 1, and the main structural parameters of **ZnPca**–**ZnPcc** taken from the calculation results are listed in Table 1. No imaginary vibration was found in the following

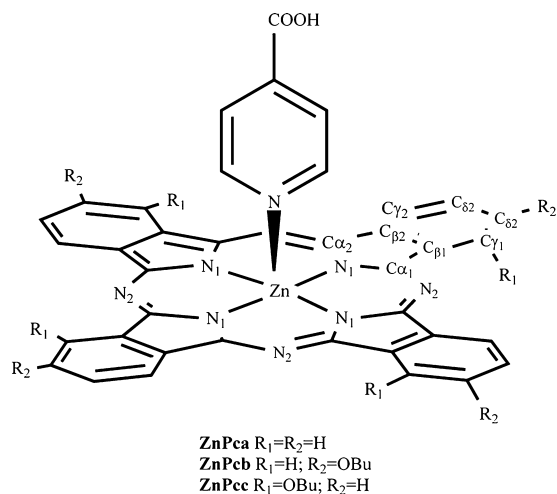


Fig. 1. Molecular structure and atom labeling of **ZnPca**, **ZnPcb** and **ZnPcc**.

frequency calculations of the three complexes, indicating that the energy minimized structures of the three complexes are at the true energy minimum.

Analysis of the calculated structural parameters for **ZnPca**, **ZnPcb** and **ZnPcc** shows that the sizes of the central hole (N–N distance) are 4.124, 4.120 and 4.124 Å, respectively. That's to say, peripheral substituents have little effect on the sizes of the central hole. The electron-donating groups at the peripheral positions does not change the circle radius formed by the four isoindole N atoms, which in complete accord with the previous research results [32]. According to our calculations, no significant change of bond length and bond angle is induced by *n*-butyoxyl groups substituted at the peripheral positions of the phthalocyanine complexes. However, the central metal Zn is further pulled out of the molecular plane by the strong attraction of the nitrogen atom according to the calculation results. At the same time, the isoindole N atoms are drawn off the primary plane of the Pc ring due to the restriction of the Zn–N bond length. It is also true for the other atoms on the phthalocyanine macrocycle. Moreover, the relative angle of 4-carboxyl pyridine relative to isoindole unit is 89.9°. Consequently, the molecular symmetry is decreased to C<sub>1</sub> for **ZnPca**, **ZnPcb** and **ZnPcc**.

Table 1

The main structural parameters (bond length/Å and bond angle/°) of **ZnPca**, **ZnPcb** and **ZnPcc** taken from the calculation results.

Parameters	ZnPca	ZnPcb	ZnPcc
Zn–N <sub>1</sub>	2.062	2.060	2.062
N <sub>1</sub> –C <sub>α1</sub>	1.389	1.388	1.386
N <sub>1</sub> –C <sub>α2</sub>	1.389	1.391	1.394
C <sub>α1</sub> –C <sub>β1</sub>	1.471	1.472	1.470
C <sub>β1</sub> –C <sub>γ1</sub>	1.403	1.403	1.403
C <sub>β2</sub> –C <sub>γ2</sub>	1.403	1.407	1.415
C <sub>γ1</sub> –C <sub>δ1</sub>	1.408	1.410	1.404
C <sub>γ2</sub> –C <sub>δ2</sub>	1.408	1.400	1.415
C <sub>δ1</sub> –C <sub>δ2</sub>	1.419	1.423	1.415
N <sub>1</sub> –Zn–N <sub>1</sub>	88.28	88.38	88.29
Zn–N <sub>1</sub> –C <sub>α1</sub>	125.37	125.45	124.52
N <sub>1</sub> –C <sub>α1</sub> –N <sub>2</sub>	127.04	127.11	127.15
N <sub>1</sub> –C <sub>α1</sub> –C <sub>β1</sub>	108.60	108.59	108.54
C <sub>α2</sub> –N <sub>2</sub> –C <sub>α1</sub>	125.58	125.66	125.80
N <sub>2</sub> –C <sub>α1</sub> –C <sub>β1</sub>	124.34	124.29	123.30
C <sub>α1</sub> –C <sub>β1</sub> –C <sub>β2</sub>	106.66	106.61	106.94
C <sub>α1</sub> –C <sub>β1</sub> –C <sub>γ1</sub>	132.24	131.49	130.42
C <sub>β1</sub> –C <sub>β2</sub> –C <sub>γ2</sub>	121.10	120.42	119.55
C <sub>β1</sub> –C <sub>γ1</sub> –C <sub>δ1</sub>	117.83	117.18	117.18
C <sub>γ1</sub> –C <sub>δ1</sub> –C <sub>δ2</sub>	121.08	121.26	121.42

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