



# Effect of substituted sites and coordinated metal atoms on the absorption properties of porphyrin and phthalocyanine derivatives



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## ABSTRACT

To design near-infrared (NIR) absorbing photosensitizing compounds, we theoretically elucidated the geometrical structures and electronic transition properties of four porphyrin-based and four phthalocyanine-based derivatives. The results show that fusion of a  $\pi$ -conjugated aromatic ring with the pyrrole rings of porphyrin can cause the larger red-shifts in the Q-bands than  $\pi$ -conjugated groups in the meso positions of porphyrin do. The extent of the red-shift of the absorption bands induced by the coordinated metal atom depends on the electrons occupied in their outer shell. The electron-donating groups also affect the absorption properties of porphyrins due to the  $\sigma \rightarrow \pi$  bond formed between the donor groups and the porphyrin ring. Based on these calculated results, we found a phthalocyanine-based compound containing Ti metal that has an absorption wavelength of 977.5 nm and a molar extinction coefficient of  $10^4$  L/mol cm. Moreover, the intrinsic reasons for the significant absorption properties for the phthalocyanine-based compounds were revealed.

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## 1. Introduction

Currently, more and more investigations are focusing on dye-sensitized solar cells (DSSCs) because they are a promising alternative to the traditional route for harvesting solar energy in an effort to address the daunting global energy crisis and environmental challenges [1–3]. In the past 20 years, the most successful dye sensitizers employed in DSSCs have been polypyridyl-type ruthenium complexes, yielding power conversion efficiencies of approximately 12% [4–6]. However, both the high cost of ruthenium and the low molar absorption coefficients are disadvantageous for Ru-pyridyl complexes applied in commercial production. Hence, extensive attention has been given to organic dyes [7,8]. Among various organic dyes, porphyrins and phthalocyanines are widely considered to be the most promising sensitizers due to the ease of modification of their structures and other useful properties. The most famous property is that the two types of compounds show intense absorptions in the near infrared (NIR) regions of the solar spectrum at 600–800 nm (Q-band) and in the near-ultraviolet regions at approximately 300–400 nm (B-band) [9].

Furthermore, they are characterized as electronic conductors and have high thermal and chemical stability, which make them suitable for widespread technological applications, such as dyes, inks, chemical sensors, photosensitizers, semiconductors, and energy conversion materials in photovoltaic and solar cells [10–13]. They show intense absorption in the visible region, as well as tunable redox potentials, presenting as promising dyes in DSSCs.

To reach high energy conversion efficiency, the dyes in DSSCs must meet a series of requirements [14,15], such as a large driving force to ensure efficient electron injection, a higher oxidation potential than that of the redox couple to guarantee fast regeneration of the oxidized dyes, and NIR absorption bands to maximize the utilized sunlight spectra (600–900 nm). Various chemical modifications of organic dyes are performed to obtain better dye properties. For instance, by introducing donor groups and  $\pi$ -conjugation in a dye molecule, a red-shifted absorption spectra and significant differences in the redox potential are achieved [16,17]. More interestingly, by coordinating a metal atom in the center of a porphyrin ring, a narrow energy gap and high absorption coefficients can be obtained [18]. The synthetic flexibility of porphyrins and phthalocyanines offers great possibilities to modify properties such as anchoring groups, the length of the connection spacer and the positions of substituted-groups. Due to the diversity of the

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molecular structures, significant time and costs are required to synthesize effective dyes. Using the theoretical molecular design of dyes to overcome experimental disadvantages is essential for the rapid construction of highly efficient DSSCs based on dyes.

The prevalent molecular design methods for effective dye sensitizers are density functional theory (DFT) and time-dependent density functional theory (TD-DFT), which can design dyes with higher absorption coefficients and broader absorption bands and reveal the intrinsic mechanism of the absorption properties [19,20]. Examples include identifying dye structures by optimizing the  $\pi$  space and the acceptor groups of dyes [21,22]. However, despite the extensive research, there are few studies on substituted positions inducing different absorption properties. The geometry, aromatic properties of the substituted groups, and metal  $d$  orbital populations will directly influence the dye adsorption and spectral response. Therefore, in the present work, in order to find porphyrin and phthalocyanine derivatives with stronger absorption bands in the NIR wavelength regions, we choose four porphyrin-based and four phthalocyanine-based compounds, that is, porphyrin ( $H_2PP$ ) and phthalocyanine (Pc) as parent molecules, respectively. The geometrical structures and electron transition properties of four  $H_2PP$ -based and four Pc-based compounds are theoretically investigated. The  $H_2PP$ -based compounds include  $H_2F_{20}TPP$  (introducing four fluorophenyl in all meso positions of porphyrin),  $PtF_{20}TPP$  (platinum coordinate with four pyrrole nitrogen atoms based on  $H_2F_{20}TPP$ ), and  $MCpTF_{20}TPP$  (a methyl-aza-cyclopentane ring fused with a pyrrole ring based on  $PtF_{20}TPP$ ). The four Pc-based compounds include  $Pc[Ph(C(CH_3)_3)]$  (butylbenzene fused with a phenyl ring in Pc),  $ZnPc[Ph(C(CH_3)_3)]$ ,  $PtPc[Ph(C(CH_3)_3)]$  and  $TiPc[Ph(C(CH_3)_3)]$  (based on  $Pc[Ph(C(CH_3)_3)]$ ). Zinc, platinum and titanium coordinate with the four pyrrole nitrogen atoms, respectively. By taking advantage of theoretical approaches, the absorption efficiency of eight conjugated macrocyclic-compounds were calculated and compared, and more appropriate substituted-positions of the functional groups were found. The relations between the absorption efficiency and substituted-positions of the functional groups were revealed, and more efficient dyes were designed. Our results strongly indicate that the theoretical molecular design could be a useful and powerful tool to design promising dye sensitizers for application in DSSCs.

## 2. Calculation methods

Density functional theory with the B3LYP [23] exchange–correlations is employed to optimize the geometric structures, calculate the vibrational frequencies and analyze the electronic structures at the ground states throughout this work. The geometric structures have been confirmed as the minima by using the vibration frequency analysis. Symmetry  $D_{2h}$  is restricted on compounds  $H_2PP$ ,  $H_2F_{20}TPP$  and  $PtF_{20}TPP$ , and  $C_{2v}$  is used for  $MCpTF_{20}TPP$ . The Pc-based compounds do not have symmetrical restrictions in this work. The electronic excitation energies and oscillator strengths are computed within the adiabatic approximation of time

dependent density functional theory [24]. For the ground state structure optimizations, the split valence plus polarization basis sets 6-31+G(d,p) for nonmetal (H, C, N, S, O) atoms and a double- $\xi$  quality LANL2DZ basis sets with the core electrons replaced by the relativistic effective core potential (ECP) of Hay and Wadt [25] for metal atoms (Pt, Zn, Ti), are used. For the electronic spectra calculations, B3LYP/6-31+G(d,p) has been employed in the TD-DFT calculation. The above calculations are implemented in a Gaussian09 software package [26] on Origin/2950 servers. The UV–Vis spectra are simulated by convolution of the first 50 excitation energy roots and corresponding oscillator strengths using the SWizard program code [27], and the peak half-width in the UV–Vis spectra is set at 0.209 eV ( $1685.83\text{ cm}^{-1}$ ) at its half-height.

## 3. Results and discussion

### 3.1. Porphyrin-based compounds

Porphyrin is a 26  $\pi$ -electron conjugated double bond molecule, which is a heterocyclic macrocycle composed of four pyrrole subunits interconnected at their  $\alpha$ -carbon atoms via methine bridges ( $=CH-$ ). The substituted porphyrin is called porphyrins. Recently, good properties of the porphyrin derivatives in the dye-sensitized solar cell have been proved by some reports [9,28,29]. To reveal the effects of the functional groups on the photophysical properties of porphyrin, four compounds with functional groups connected at different positions of porphyrin are investigated, as shown in Fig. 1, where  $H_2PP$  is porphyrin itself.  $H_2F_{20}TPP$  is a *meso*-substituted porphyrin-based molecule, four fluorophenyls are as *meso*-substituted groups based on the stability and the low toxicity consideration. Four central nitrogen atoms of  $H_2F_{20}TPP$  coordinate with Pt, resulting in  $PtF_{20}TPP$ . Compared with  $PtF_{20}TPP$ , there is a methyl-aza-cyclopentane ring fused with a pyrrole ring in  $MCpTF_{20}TPP$ . In the following discussion, the most stable structures, absorption spectra and frontier orbital properties of the four porphyrin-based compounds are investigated in detail.

#### 3.1.1. Optimized geometrical structures of porphyrin-based compounds

The ground state structures of the four porphyrin-based compounds are optimized by the B3LYP/6-31+G(d,p) method (LANL2DZ basis sets for Pt). Apart from  $MCpTF_{20}TPP$ , which shows  $C_{2v}$  symmetry, the other three compounds,  $H_2PP$ ,  $H_2F_{20}TPP$  and  $PtF_{20}TPP$ , exhibit  $D_{2h}$  symmetry. The optimized structures of the four compounds are shown in the supporting information I. The main structural parameters of the four compounds are shown in Table 1. From Table 1, it can be seen that the C–N bond in the pyrrole ring is almost 1.39 Å. There are two types of C–C bonds (1.44 and 1.38 Å) in the pyrrole ring. The bond length of C(9)–C(17) is 1.50 Å, and it is formed by a methine carbon and fluorophenyl carbon atoms. The three angles formed by C17, C8 and C10 around C9 are 125°, 118°, and 117°, respectively, which are nearly 120°. Consequently, a deformed equilateral triangle is formed by carbon

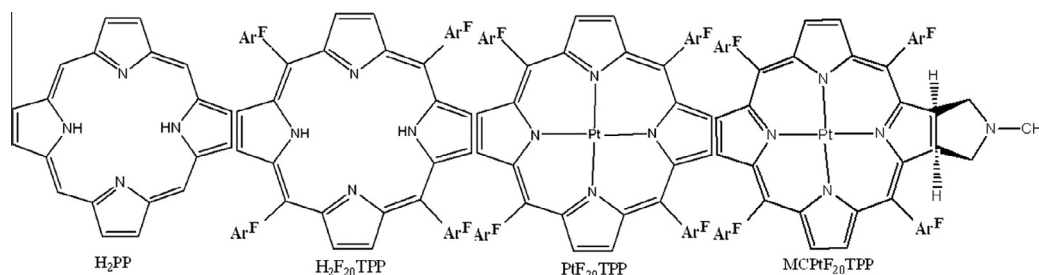


Fig. 1. Molecular structures of the four porphyrin-based compounds.

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