



A density functional theory study on photophysical properties of red light-emitting materials: Meso-substituted porphyrins

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ABSTRACT

The density functional theory (DFT) has been applied to investigate the photophysical properties of meso-substituted porphyrins: 5,15-difluorenylporphyrin (DFP), 5,10,15,20-tetrafluorenylporphyrin (TFP), Zn-5,10,15,20-tetrafluorenylporphyrin (FPZ) and Zn-5,10,15,20-tetrafluorenoneporphyrin (OPZ). The geometry structures, frontier molecular orbitals, ionization potential (IP), electron affinity (EA) and reorganization energy (λ) together with the absorption and emission wavelengths of these compounds were investigated. Theoretical calculations indicated that the introduction of meso-substitutions brought about significant effect on the photophysical properties. The TFP molecule has lowest hole injection energy barrier of all the studied compounds, and OPZ owns lowest electron injection energy barrier of them. The equilibrium of the hole and electron transport of FPZ is better than those of porphyrin (FBP), DPZ, TFP, and OPZ. The electron reorganization energies ($\lambda_{\text{electron}}$) of FBP, DFP, TFP, FPZ and OPZ are 0.22 eV, 0.20 eV, 0.23 eV, 0.26 eV and 0.13 eV, respectively, which are smaller than tris(8-hydroxyquinolino) aluminum(III), thus these molecules are potential electron transport materials. Their visible absorption wavelengths are calculated by TD-B3LYP and semi-empirical ZINDO methods, and these results agree with corresponding experimental values. The fluorescence spectra of these complexes predicted by TD-HF method exhibit more consistent results with experimental data than by TD-B3LYP method.

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1. Introduction

Since the early work of Tang and VanSlyke [1], organic light-emitting diodes (OLEDs) have attracted tremendous attention in application to the large-area flat-panel display devices. Normally, OLED devices are comprised by three layers: the electron transport layer, the emitter layer, and hole transport layer. Holes are injected from anode into the hole transport layer then migrate toward emitter layer, while electrons are injected from cathode into the electron transport layer then migrate toward emitter layer. Once they recombine in the emitter layer, the excitons are produced. Therefore, the balance of charge-carrier transport rate is very important for high efficiency OLEDs.

Nowadays, a new type of nondopant red light-emitting materials has emerged [2–6], in which 5,15-difluorenylporphyrin (DFP), 5,10,15,20-tetrafluorenylporphyrin (TFP), Zn-5,10,15,20-tetrafluorenylporphyrin (FPZ) and Zn-5,10,15,20-tetrafluorenoneporphyrin (OPZ) (as depicted in Fig. 1) reported by Paul-Roth [5,6] exhibit good red chromaticity and enhanced emission efficiency, as well as higher fluorescence quantum yield

than many other porphyrins [7] and Zn porphyrins [8]. However, there has been no report on the efficiency of carrier injection and transport properties. And it is also uncertain whether these compounds can function as electron transport materials (ETM), hole transport materials (HTM) or emitter materials (EM). Therefore, this contribution will present a systematical theoretical investigation on the electronic structures, electronic spectra, especially for the charge injection and transport properties of DFP, TFP, FPZ and OPZ. We calculated the ionization potential (IP) and electronic affinity (EA) to evaluate the energy barrier for injection holes and electrons, and also computed reorganization energy (λ) to investigate the charge transport on the Marcus electron transfer theory [9]. And all the calculated values were compared with the attainable experimental data to testify the theoretical methods.

2. Computational methods

Density functional theory (DFT) has been widely used in π -conjugated systems including porphyrins, and these results are more accurate than those derived from other methods [10–13]. It is known that due to the self-interaction error in DFT and subsequent wrong asymptotic behavior of the potential, in quantitative terms, DFT orbital energies are in much poorer agreement with photoelectron spectra than HF IPs by Koopmans Theory. However, DFT

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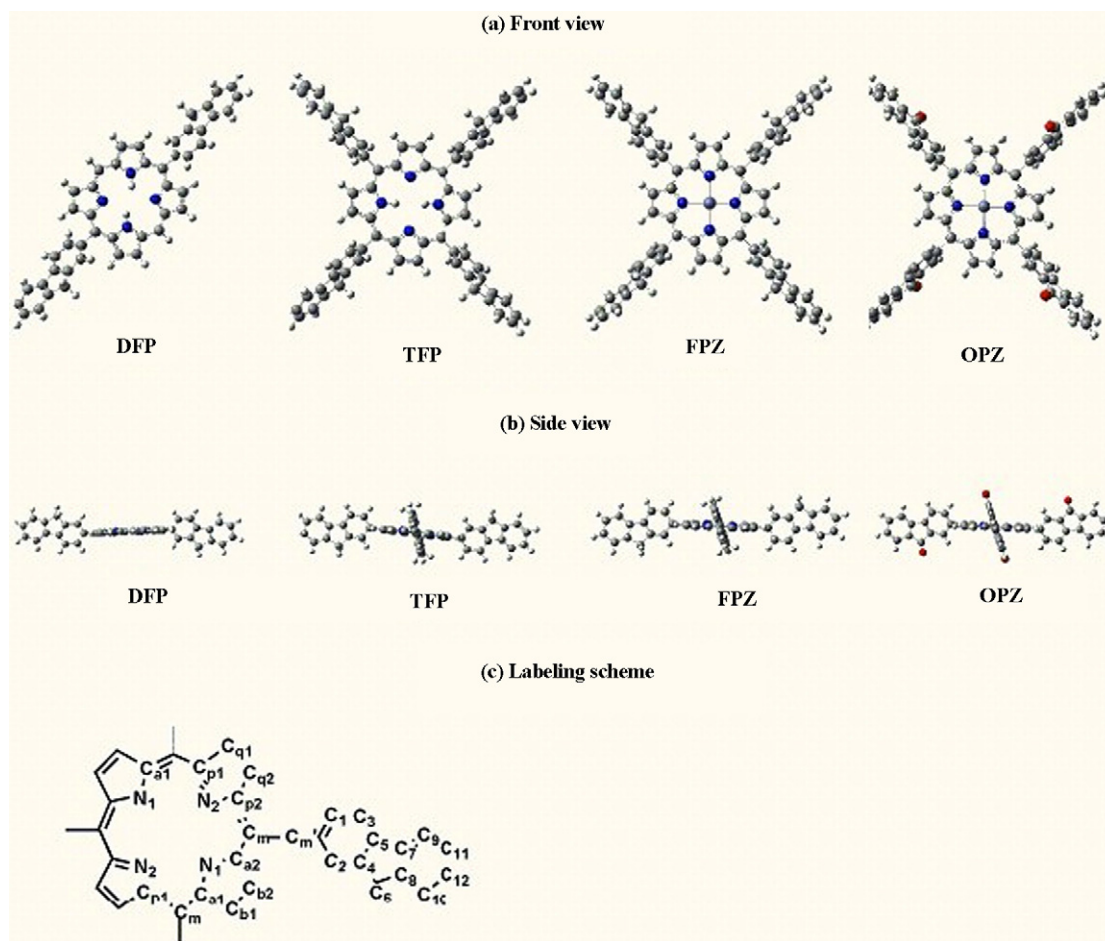


Fig. 1. (a) Front view of the optimized structures of DFP, TFP, FPZ and OPZ obtained by DFT//B3LYP/6-31G(d); (b) side view of them; (c) labeling scheme for all the meso-substituted-porphyrins (especially for FPZ and OPZ, Zn is connected with N₁ and N₂ in the center of porphyrin).

can excellently predict to the lowest energy state as well as the IP and EA by Δ SCF method (i.e. IP/EA value is obtained by the energy difference between the cationic/anionic and neutral states). Thus all the geometries optimization of these compounds in their neutral, cationic and anionic states were calculated by Beck's three parameters hybrid functional (B3LYP) [14–16] with 6-31G(d) basis sets. The neutral, cationic and anionic forms of these compounds were used to compute the IP and EA, hole extraction potentials (HEP), electron extraction potentials (EEP) and reorganization energy (λ). On the basis of the optimized ground state geometries, the electronic absorption spectra were investigated by the TD-B3LYP and ZINDO [17] methods. Considering the large size of these molecules and available computational resources, the lowest singlet excited state structures were calculated with ab initio CIS/3-21G(d). Following these optimized excited structures, the fluorescence spectra were calculated by the TD-HF and TD-B3LYP methods. All the above calculations were performed on the SGI origin 2000 server, using Gaussian03 program package [18].

3. Results and discussion

3.1. Neutral and ionic geometry structures

The molecular structures and atoms labeling scheme are depicted in Fig. 1, and main optimized geometry structural parameters are collected in Table 1. Compared with porphyrin (FBP), the introductions of fluorenyl and fluorenone fragments have slightly drawn C_m away from porphyrin core, which result in lengthened

C_{α1}–C_m, C_{α2}–C_m, C_{p1}–C_m and C_{p2}–C_m bond lengths. Table 1 also shows that the main structure parameters of DFP are similar with TFP. The maximum deviations are found in the C_{α2}–C_m, C_{p2}–C_m bond lengths. And OPZ has similar geometrical and electronic structures with FPZ. According to the NBO analyses, the charge population of fluorenyl and fluorenone are 0.0148 and 0.0164 a.u., respectively, which indicates that the ability of electron-donation of fluorenyl is similar with that of fluorenone. After Zn atom is chelated at the pyrrole ring, the bond lengths in porphyrin ring have changed. The C_{a1}–C_{b1}, C_{a2}–C_{b2}, C_{p1}–N₂, C_{p2}–N₂ bond lengths of FPZ increase by about 0.010 Å than those of TFP, and C_{p1}–C_{q1}, C_{p2}–C_{q2} bond lengths of FPZ decrease by about 0.015 Å than those of TFP.

From side view of the studies molecules, the porphyrin rings are near in plane. Since the repulsion of hydrogen's between C_{q1}–H/C_{b1}–H and C₁–H/C₂–H, the dihedral angles α (C₁–C_m–C_m–C_{a2}) between substitutions plane (fluorenyl or fluorenone) and porphyrin-ring plane are 61.9°, 67.8°, 69.1°, 68.6° for DFP, TFP, FPZ, OPZ, respectively. The large inter-angles are considered as the structural feature of energy-transfer systems [19].

The bond lengths deviations between the ionic and its corresponding neutral states are drawn in Fig. 2. It is clear that the larger variations in different states mainly focus on porphyrin ring. As shown in Fig. 2, for DFP, in the cationic state, the inter-ring distance C_m'–C_m (labeled 15) decreases by 0.020 Å and the C_{a1}–C_m (labeled 5) increases by 0.013 Å. In the anionic state, the inter-ring distance C_m'–C_m decreases by 0.015 Å, and C_{p2}–N₂ (labeled 11) and C_{p2}–C_m (labeled 13) increase by 0.015 Å. Similarly, for TFP, in

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