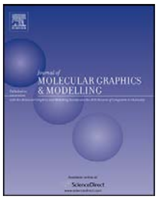
Journal of Molecular Graphics and Modelling 29 (2011) 717–725

Contents lists available at ScienceDirect

Journal of Molecular Graphics and Modelling

journal homepage: www.elsevier.com/locate/JMGM



Density functional theory studies on the structures and electronic communication of *meso*-ferrocenylporphyrins: Long range orbital coupling *via* porphyrin core

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ARTICLE INFO

Article history:
Received 14 September 2010
Received in revised form 5 December 2010
Accepted 7 December 2010
Available online 17 December 2010

Keywords:
Density functional theory
Meso-attached ferrocenylporphyrins
Molecular orbital
Long range electronic coupling
Electronic absorption spectra

ABSTRACT

The molecular and electronic structures together with the electronic absorption spectra of a series of metal free *meso*-ferrocenylporphyrins, namely 5-ferrocenylporphyrin (**1**), 5,10-diferrocenylporphyrin (**2**), 5,15-diferrocenylporphyrin (**3**), 5,10,15-triferrocenylporphyrin (**4**), and 5,10,15,20-tetraferrocenylporphyrin (**5**) have been studied with the density functional theory (DFT) and time-dependent density functional theory (TD-DFT) methods. For the purpose of comparative studies, metal free porphyrin without any ferrocenyl group (**0**) and isolated ferrocene (**6**) were also calculated. The effects of the number and position of *meso*-attached ferrocenyl substituents on their molecular and electronic structures, atomic charges, molecular orbitals, and electronic absorption spectra of **1**–**5** were systematically investigated. The orbital coupling is investigated in detail, explaining well the long range coupling of ferrocenyl substituents connected *via* porphyrin core and the systematic change in the electronic absorption spectra of porphyrin compounds.

1. Introduction

Discrete molecular systems containing multiple photo- and redox-active centers with long range electronic coupling have received considerable attention in recent years due to their potential applications in molecular electronic devices [1–4]. Ferrocene has been widely used in the construction of such multi-component systems for the purpose of detecting and investigating the metal–metal coupling due to its unique structural and well-defined redox behavior [5–7]. Porphyrins [8–12] and their most important artificial analogues, phthalocyanines [13], are ideal frameworks linking the redox-active metallocenyl units including ferrocenyl substituents due to their special molecular structure, electrochemical, and photophysical properties. For the purpose of constructing novel supermolecular structures with novel multi-functional properties, combination of these two functional subunits, i.e. porphyrin core and ferrocenyl unit(s), has attracted increasing research interest since last century [14,15].

Experimental investigations have revealed that effective long range electronic coupling between ferrocenyl units linked *via* porphyrin framework was retarded to some degree probably by the not close enough distance and unsuitable relative orientation due to the unlimited free rotation of the ferrocenyl units [12,15,16]. This, however, has not yet been confirmed from the point of theoretical investigation because of the lack of theoretical calculations in this regard. On the other hand, density functional theory (DFT) and time dependant density functional theory (TD-DFT) methods have proved suitable for the calculation of the energy-minimized structures, electronic distribution, molecular orbitals, electron transfer, and electronic absorption spectra of a series of porphyrin and phthalocyanine derivatives [17–23] as well as ferrocene derivatives [24–29]. As a consequence, towards understanding the long range electronic coupling between ferrocenyl groups connected *via* porphyrin framework, theoretical studies over multi-component compounds composed of porphyrin and ferrocenyl units appear interesting. It is worth noting that during review process of the present paper, Nemykin et al. synthesized and characterized a series of free-based *meso*-poly(ferrocenyl)-containing porphyrin [30] and studied the electron absorption spectra of these series compounds with DFT method [31], which provide a good chance for comparing our calculation result with the experimental and previous computational data despite that detailed studies on the electronic structures and orbital coupling of the series of compounds were not included.

In the present paper, density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations were carried out on the basis of the molecular and electronic structures, interaction between the porphyrin core and ferrocenyl substituent(s), long range electronic interaction

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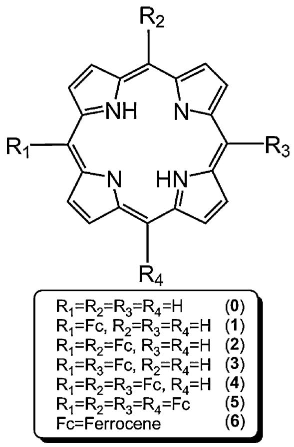
doi:10.1016/j.jmgm.2010.12.006



Scheme 1. Schematic molecular structures of **0**–**6**.

between ferrocenyl groups, and electronic absorption spectra of a series of metal free *meso*-ferrocenylporphyrins, namely 5-ferrocenylporphyrin (**1**), 5,10-diferrocenylporphyrin (**2**), 5,15-diferrocenylporphyrin (**3**), 5,10,15-triferrocenylporphyrin (**4**), and 5,10,15,20-tetraferrocenylporphyrin (**5**), Scheme 1. For the purpose of comparative studies, metal free porphyrin without any ferrocenyl group (**0**) and isolated ferrocene (**6**) molecule were also calculated.

2. Computational details

Density functional theory (DFT) method of hybrid B3LYP [32,33] functional with Becke exchange and Lee–Yang–Parr correlation was used to calculate the molecular structures of the series of *meso*-ferrocenyl porphyrins. The LACVP(d) basis set [34,35], which is a combination of the 6-31G(d) basis set for C/H/N with the LanL2DZ effective core basis set for Fe, was chosen. The B3LYP functional method with LACVP(d) basis set is proved suitable for geometry optimizations of porphyrins [17–20] and ferrocenyl-containing systems [28,29]. The Berny algorithm using redundant internal coordinates [36] was employed in energy minimization and the default cutoffs were used throughout. No imaginary vibration is predicated in the following frequency calculations of the IR vibration spectroscopy, indicating that the energy-minimized structures for all of the complexes are true energy minima. Natural bond orbital (NBO) analysis [37] was carried out with NBO 3.1 [38] in Gaussian 03 program [39] on the basis of the minimized structures.

The electronic structures and electronic absorption spectra were calculated using DFT method of Beck's exchange functional [32] and Perdew–Wang correlation functional (BPW91) [40]. The 6-311+G(d) basis set for Fe atom and 6-311G(d) basis set for all other atoms was employed. All calculations were carried out using the Gaussian 03 program [39] on an IBM P690 system housed at Shandong Province High Performance Computing Center.

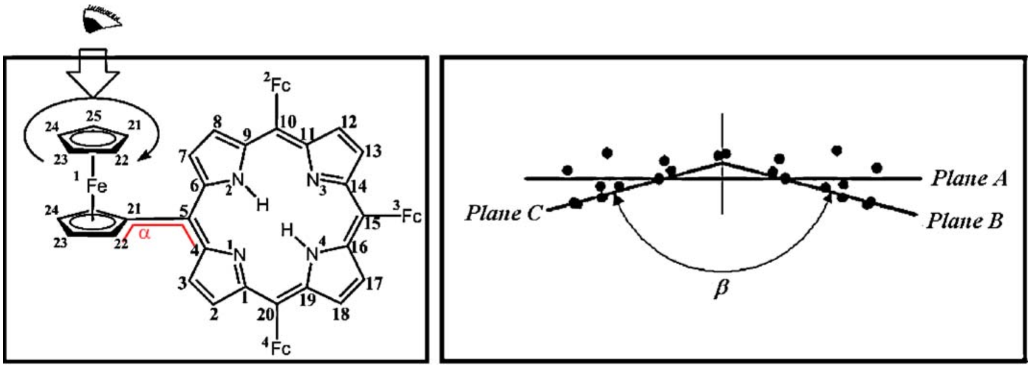
The total electron density difference between ground and excited states ($\sum f_{m\to n}$) is calculated by the molecular orbital electron density difference with formula $f_{m\to n} = (c^2_{m\to n}/\sum c^2_{m\to n})(\rho_n - \rho_m)$, where ρ_n and ρ_m are the electron density of the two molecular orbitals relative to the electron transition model of MO(m) → MO(n), $c_{m\to n}$ is the orthogonal coefficient in the TD-DFT equation, and then $(c^2_{m\to n}/\sum c^2_{m\to n})$ can be considered as the contribution of this electron transition model to this absorption peak. The electron density difference between ground and excited states is the linear combination of various electron transition models. Also for the reason of time efficiency, only the electron transition models with the configuration larger than 5.0% are taken into account. The electron density difference map is plotted using the isovalue of 4.0×10^{-4} e au^3.

3. Results and discussion

3.1. Molecular structures

Table S1 (Supporting Information) compares the calculated structural parameters of **5** with those revealed by single crystal X-ray diffraction analysis [30]. As can be found, the largest difference of atom distance and bond angle for ferrocenyl substituents between the calculated and experimental data is only 0.06 Å for Fe–C22 and 0.7° for C28–C29–C30 in **5**, respectively, indicating the reliable simulated molecular structures at the level of B3LYP/LACVP(d).

In the metal free porphyrin without any ferrocenyl unit **0**, the central porphyrin core possesses a complete planar structure. However, as can be found in Table 1, the original planar porphyrin core becomes distorted due to the introduction of ferrocenyl substituent(s) onto the *meso*-positions of porphyrin ring. As shown in Scheme 2, the torsion angle β defined as the dihedral angle between plane B (defined by N1, N4, and C20) and plane C (defined by N3, N2, and C10) is employed to describe the nonplanarity for the porphyrin core of *meso*-ferrocenylporphyrins **1**–**5**. Along with the increase in the *meso*-attached ferrocenyl groups from one, two, three, to four for **1**, **2** (**3**), **4**, and **5**, the torsion angle β increases from 6.3, 13.5 (11.7), 22.4, to 30.6°, revealing the increased distortion of the porphyrin core in the same order due to the increased steric hindrance, Table 1. Nevertheless, an excellent linear relationship exists between the torsion angle (and the number of *meso*-attached ferrocenyl substituents, Fig. S1 (Supporting Information).



Scheme 2. Atom labeling of **5** as a typical representative. Inclination angle C22–C21–C5–C4 (α) shows the torsion angle between ferrocenyl units and porphyrin core. Plane A is the average plane of the four inner nitrogen atoms. Plane B is defined by N1, N4 and C20. Plane C is defined by N3, N2, and C10. Torsion angle β is the dihedral angel between plane B and plane C.