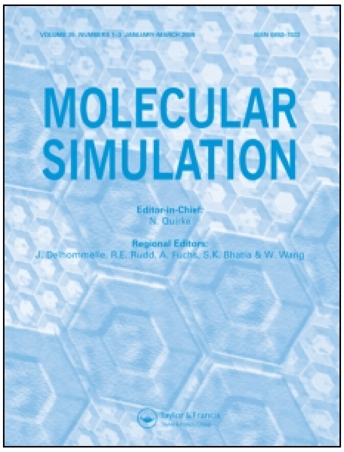

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Structure and Electronic Properties of Metal Di-(4-thiophenyl)-porphyrin

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The geometry and electronic structures of metal 5, 15-di-(4-thiophenyl)-porphyrin (MDTP) have been investigated using first-principles calculations. Several metal atoms, including Cr, Mn, Fe, Co, Ni, Cu and Zn, have been selected. It has been found that the dihedral angle between porphyrin and thiophenyl planes is close to the perpendicular, which means that the π conjugation in whole MDTP molecules is broken. The most stable spin configurations of Cr, Mn, Fe, Co and NiDTPs are $S = 2$, 5/2, 1, 1/2 and 0, respectively. Analysis of metal 3d-orbital splitting in Zn and NiDTP have shown that in the case of NiDTP, the out-of-plane interaction between metal 3d-orbitals and π orbital of porphyrin is larger than that in the case of ZnDTP. The results suggest that the Ni metal will enhance the conductance of DTP because transport properties in molecular systems have strong relations to the molecular π orbital.

Keywords: Metal porphyrin; Transport properties; First-principles calculations; 3d-orbital splitting

INTRODUCTION

Recently, the research field of the molecular electronics has advanced significantly with many experiments that probe the behavior of small groups of molecules, such as scanning probe microscope (SPM) technology [1]. It will make it possible to construct a molecular wire, molecular rectifier and other functional devices using a finite number of self-assembled molecules or even just single molecules in the near future. The theoretical studies are also important part of the molecular electronics because they can directly propose and design novel nanodevices as well as enrich the experimental intuition. For example, molecular electronics dates back to the original theoretical work in which Aviram and Ratner revealed the possibility of an organic molecule functioning as a molecular rectifier [2].

Theoretical studies have been mainly dedicated to the understanding of conduction mechanisms through different molecular systems [3–4] and how the electronic structure of the molecule and the geometry of the molecule/metal interface affect the conduction characteristics [5–6]. The porphyrin molecule is one of the most promising candidates for future nanoelectronic devices because it can be used as a building block in complex molecular circuits. This is supported by a recent discovery that different porphyrin arrays having rigid geometric structure and stability in air [7]. Using such arrays it is possible to control the π orbital delocalization which is desirable for molecular wire applications. Moreover, such porphyrin polymers can be doped by different kind of metals that can increase the opportunity to use these polymers in spintronics.

In this paper, we investigate the structures and electronic properties of different metal-containing porphyrin molecules by using first-principles calculations. The influence of the different metal atoms on electronic transport through the porphyrin core has been also analyzed.

METHOD

In this study we consider a porphyrin molecule with two thiophenyl substituents at its right and left sides, respectively, because the thiol-type sulfur atom has widely been used as the alligator clip for the connection to Au electrodes. We examine the structure and electronic properties of both

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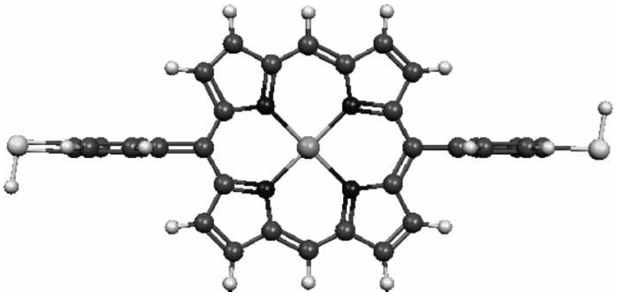

FIGURE 1 Structure of MDTP (M = Cr, Mn, Fe, Co, Ni, Cu, and Zn).

undoped socalled free-based (FB), and metal-doped porphyrins (see Fig. 1). Seven first-row transition-metal complexes (from Cr to Zn) of 5,15-di-(4-thiophenyl)- porphyrin (MDTP), were selected for the investigation.

The geometry optimization of MDTPs has been performed by using density functional theory (DFT) coupled with B3LYP exchange-correlation functions. Moreover, the most stable spin configurations of MDTPs (M = Cr, Mn, Fe, Co, and Ni) have been examined and only the most stable spin configurations have been selected for the consideration. It is well-known that the density functional approximation (for example, BLYP) cannot reproduce the energy of excited state, and always gives the underestimated value as compared with the experimental one. The introduction of a hybrid functional in the DFT formalism gives a larger value as compared with a pure DFT one. Moreover, the B3LYP functional within the time-dependent DFT has been shown to produce low-lying excitation energies that are in excellent agreement with experimental results for porphyrins [8]. It has also been found that the optimization geometry of Zinc tetraphenylporphyrine (ZnTPP) better reproduces the experimental structure by B3LYP functional than by BLYP functional. We used the 6-311G and 6-31G(d) basis sets. The 6-311G basis set is commonly used for the prediction of the electronic structure of the first transition-row complexes, especially Fe [9], and therefore, it is mostly used in present study. For comparison, the 6-31G(d) basis set has been also applied in order to verify the obtained calculated results. All calculations were carried out using Gaussian 98 set of programs [10].

RESULTS AND DISCUSSION

First, we determined geometries of MDTPs. It has been found that the dihedral angle between the porphyrin ring and thiophenyl group is nearly perpendicular. Although it is well known that the phenyl ring at the meso-position prefers perpendicular conformation, the results for the thiophenyl group may be interesting from the experimental point of view, especially the energy difference between planar and perpendicular conformations. For instance, in order to gain accurate measurements of transport through these molecular structures, they should properly adsorb on metal contacts. Figure 2 shows the energy difference of ZnDTP as related to the most stable structure as a function of the rotation angle of the thiophenyl substituents. Moreover, the torsional potential of ZnTPP has been also calculated.

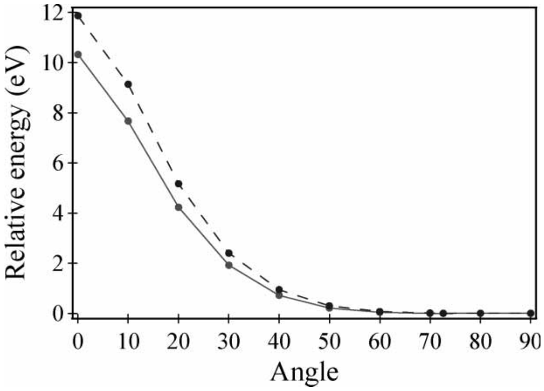

FIGURE 2 Relative energy of ZnDTP (solid) and ZnTPP (dashed) as a function of dihedral angle between porphyrin plane and thiophenyl groups.

As expected, from this figure it is clear that the near-perpendicular conformation of meso-substituent is the most stable, while the planar conformation has the highest energy, with the energy difference about 10.3 eV. The energetically favorable perpendicular conformation leads to the destruction of the $\pi-\pi$ interaction between the porphyrin core and meso-substituents and thus to the reduction of the electron transport properties in this system. It is also interesting to note that there is no significant change in energy, when the torsion angle between meso-phenyl group and porphyrin core varied from 70° to 90°. In other words, the perpendicular conformation is flexible and can be easily changed to a near-perpendicular one under external perturbation such as temperature. The same tendency of change of torsional potential has been observed in ZnTPP (see Fig. 2). The only difference is in the value of relative energy, which is slightly higher than that in the case of ZnDTP, ranging from 0° to 60°. This can explain the dispersion of experimental data which reported near-perpendicular position of phenyl group with different absolute values of dihedral angle.

The geometry of the ZnTPP has been calculated using both B3LYP/6-311G and BLYP/6-31G(d) theory levels. The calculated Zn–N distance is found to be 2.047 and 2.061 Å using B3LYP and BLYP functionals, respectively. The obtained B3LYP result is more close to the experimental one (2.045 Å) [11] than that obtained by BLYP level. The optimized M–N bond lengths for the various MDTPs are collected in Table I

TABLE I Calculated and available experimental M–N bond lengths (Å) in MDTP

Stable spin configuration	*Present study B3LYP/6-311G*	*Experimental data*
CrDTP ($S = 2$)	2.045	–
MnDTP ($S = 5/2$)	2.087	–
FeDTP ($S = 1$)	1.999	1.972 [12]
CoDTP ($S = 1/2$)	1.986	1.949 [13]
NiDTP ($S = 0$)	1.971	1.930 [14]
CuDTP ($S = 1/2$)	2.016	1.981 [15]
ZnDTP ($S = 0$)	2.048	2.042 [15]

TABLE II Relative energy (eV) of MDTPs as calculated for the various spin states using B3LYP/6-311G and B3LYP/6-31G(d) (in parentheses) methods

	$S = 0$	$S = 1$	$S = 2$
CrDTP	2.84 (2.94)	1.97 (2.02)	0
FeDTP	1.53 (1.59)	0	0.21 (0.14)
NiDTP	0	0.51 (0.45)	–
	$S = 1/2$	$S = 3/2$	$S = 5/2$
MnDTP	0.97 (1.18)	0.16 (0.41)	0
CoDTP	0	0.20 (0.12)	–

Zero value indicates the energetically most stable spin configuration.

together with the experimental data for meso-tetraphenyl porphyrins (MTPP) [12–15]. The calculated M–N distances in CoDTP and NiDTP are close to 1.98 Å. That is, shorter than those in ZnDTP, MnDTP, and CrDTP, which are around 2.07 Å. The bonds between carbon and nitrogen atoms in pyrrole rings are practically the same for different MDTPs. The agreement between the calculated and available experimental data is quite good with the largest deviation of 0.04 Å. Accordingly, it is confirmed that the selected calculation method accurately predicts the structural properties of studied molecules.

The most stable spin configuration for each of MDTPs has been determined by the comparison of the total energy of optimized MDTP structures with the different spin configurations. At the first step, we have calculated the most stable spin configuration of FeTPP using B3LYP/6-311G level and compared with available theoretical and experimental data in order to make sure that the selected method can accurately predict the magnetic state of metal in metalporphyrin complexes. The most stable spin configuration of FeTPP has total spin $S = 1$. The state with $S = 2$ lies 0.51 eV above most stable spin configuration and in comparison with a magnetic susceptibility measurement that yielded a value of 0.62 eV [16]. The lowest closed-shell state ($S = 0$) lies 0.98 eV above the ground state. The recently obtained theoretical results are showed the same tendency magnetic configuration of FeTPP. The most stable spin configuration ($S = 1$) and the energy difference between this spin state and other configurations ($S = 2$ and $S = 0$) are found to be 0.75 and 1.15 eV, respectively [17].

Table II shows the difference in total energy for each of the spin configurations as related to the total energy of the most stable configuration defined as 0. Symbol S indicates the total spin of the system, which is the difference between the number of spin-up and spin-down electrons. CuDTP and ZnDTP have only one spin configuration, $S = 1/2$ and $S = 0$, respectively. In the cases of Cr, Mn, Fe, Co, and NiDTPs, the most stable spin configurations are $S = 2$, $5/2$, 1, $1/2$, and 0, respectively. These are in an agreement both with the theoretical [17] and experimental results [12,18,19] obtained for the metal-containing MTPP. The smaller energy difference between the lowest electronic configurations for the triplet and quintet states in FeDTP (0.21 eV) as compared to that in FeTPP (0.75 eV [17]), can be explained by the reduction of the molecular symmetry from D_{4h} in FeTPP to C_{2h} in FeDTP. It can be seen that both basis sets can predict the most stable spin configuration of different metalporphyrin complexes. However, in some cases (Fe and Co), the results obtained by 6-31G(d) show smaller energy differences between different spin configurations than that in the case of the 6-311G basis set. Therefore, the 6-311G basis set is more reliable to predict the spin configurations of Fe and CoDTP complexes.

The calculated large energy difference between the different spin configurations in the Mn, Fe, and Cr complexes suggest that these compounds can be used as a building blocks in the spintronic devices.

It is well known that the stronger the π orbital overlap in the system, the better its electron transport properties [2]. Thus, we investigated 3d-orbital splitting of different central metal atoms by porphyrin ligand field in order to understand the effect of out- and in-pane metal-ligand interactions on the conductance properties of MDTP. Theoretically, there are two possible 3d-orbital splitting by the square-planar ligand field. First, is an in-plane splitting scheme, which reflects a dominant in-plane interaction between the metal 3d($d_{x^2-y^2}$ and in part d_{z^2}) orbitals with porphyrin σ-donor orbitals. The second case is an out-of-plane splitting scheme, which reflects a dominant out-of-plane interaction between the metal 3d(d_{xz}, d_{yz}, d_{xy}) orbitals and π-donor or acceptor orbitals of the porphyrin ligand. Figure 3 shows the 3d orbital order for both cases.

Table III and IV show 3d-metal orbital splitting, in the case of ZnDTP and NiDTP complexes, respectively. Both of these structures have zero-spin configurations but the interactions between these metals and porphyrin ligand are different.

From these tables it has been seen that the 3d-orbital splitting has predominantly in-plane

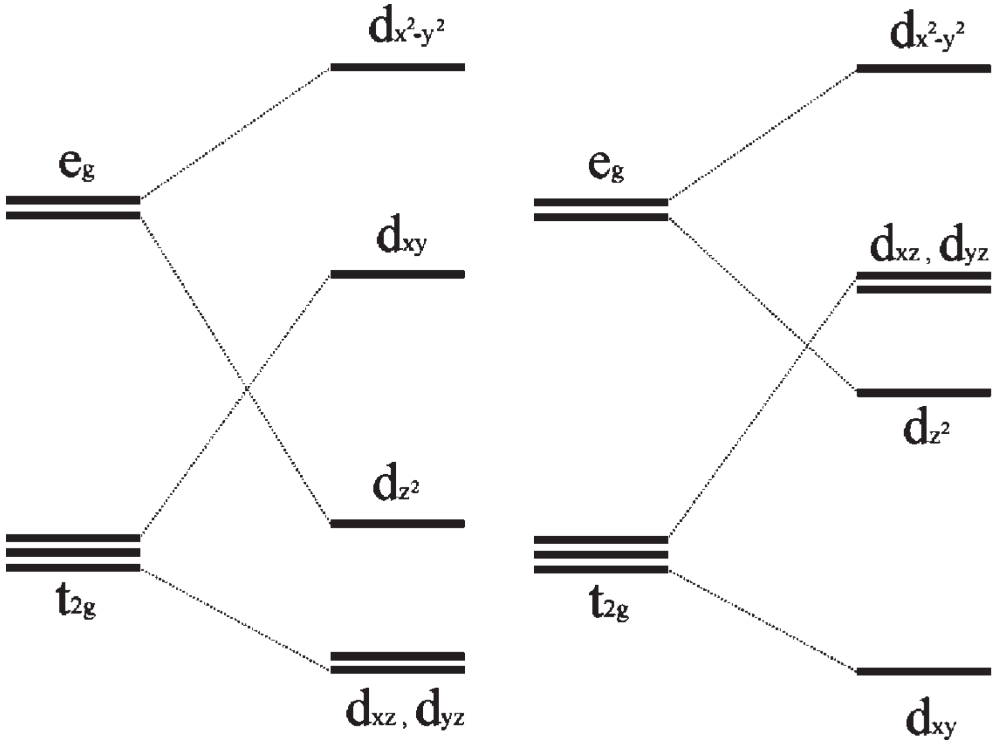

FIGURE 3 Schematic diagram of 3d metal orbital splitting in the square-planar ligand field: (a) in-plane and (b) out-of-plane.

character in the case of ZnDTP, while it is predominantly out-of-plane splitting in the case of NiDTP. Thus Zn has strong σ-type interactions with the porphyrin core, while Ni has strong π-type interactions with the porphyrin core. Moreover, the orbitals close to the HOMO–LUMO gap play a main role in conductance properties through the molecule. The analysis of the electronic structure shows that the predominantly metal-centred occupied molecular orbitals are shifted to the lower energy in the MO diagram. Thus, in the case of ZnDTP, the orbitals with metal contribution lie lower than in the case of NiDTP. In the case of NiDTP, the $d_{x^2-y^2}$ is unoccupied orbital (LUMO + 2) while d_π and d_{z^2} are close to HOMO (see Table IV). Moreover, the absence of electron in $d_{x^2-y^2}$ orbital results in shorter distance between Ni and N and therefore the better overlap between the orbitals of porphyrin ring is larger in this case as compared to the ZnDTP, where all the 3d orbitals of metal are filled. All of these results can verify that the expected conductance of NiDTP should be larger than that in ZnDTP.

SUMMARY

In this paper the structural and electronic properties of various MDTPs (M = Cr, Mn, Fe, Co, Ni, Cu, and Zn) were studied by using the DFT method. It was found that the stable structure of MDTP has near perpendicular dihedral angle between porphyrin and thiophenyl planes. The most stable spin states for Cr, Mn, Fe, Co, and NiDTPs are $S = 2$, $5/2$, 1, $1/2$, and 0, respectively. The analysis of 3d-orbital splitting shows that different metal atoms have different contributions in π out-of-plane orbitals. The results imply that incorporation of the Ni into the porphyrin may enhance the transport properties larger than incorporation of the Zn. Moreover, the thyophenyl groups conformation leads to the elimination of the π conjugation in whole MDTP structures and other connections of porphyrin to electrodes should be proposed in order to realize the molecular wire for the interconnections between electronic devices.

TABLE III 3d-metal orbital splitting of ZnDTP

Molecular orbital	*3d-metal orbital*	*Energy level (eV)*
HOMO-2	$d_{x^2-y^2}$	− 6.69
HOMO-24	d_{xy}	− 10.32
HOMO-25	d_{z^2}	− 10.50
HOMO-34	d_{yz}	− 11.22
HOMO-35	d_{xz}	− 11.28

TABLE IV 3d-metal orbital splitting of NiDTP

Molecular orbital	*3d-metal orbital*	*Energy level (eV)*
LUMO + 2	$d_{x^2-y^2}$	− 1.61
HOMO-2	d_{yz}	− 6.22
HOMO-3	d_{xz}	− 6.24
HOMO-4	d_{z^2}	− 6.33
HOMO-17	d_{xy}	− 8.10

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