STRUCTURE OF MATTER
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Thermodynamic Stability and Electron Structure of Polymeric Sandwich Complexes of Porphyrins with Different Metals

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Abstract—The thermodynamic stability of different conformers of the polymeric sandwich structures of metalloporphyrins (MeP) is studied by means of quantum chemistry. The possibility of forming stable layered BaP, SrP, ScP, YP, and ZrP structures with shielded and retarded conformation is demonstrated. Shielded conformers are preferable in the case of SrP, BaP, and ScP complexes, while retarded conformers are most advantageous for YP and ZrP complexes. Based on the results from calculating the electron structure of the investigated compounds, we find that SrP and BaP are semiconductors and ScP, YP, and ZrP are electrical conductors

INTRODUCTION

Porphyrins (P) belong to the class of environmentally friendly materials found in abundance in nature. The structure of complexes prepared on their basis opens up new possibilities for varying their properties by introducing additional functional groups into the porphyrin molecules, and by choosing the central ion of metal in the coordination sphere of a heterocycle [1]. These structural features make porphyrins promising materials in the field of molecular design.

A tetrapyrrole macrocycle has unique properties of chelation, and a rich variety of porphyrin complexes with various elements has therefore been obtained. Porphyrin ligands with an N_4 coordination cavity having a radius of ~2 Å generally form extremely stable coordination compounds with metal ions. A metal ion migrating to the center of the macrocycle cavity forms an MN_4 coordination center. A cation either occupies the center of the N_4 plane, forming MN_4 coordination center, or it turns out to be elevated over the plane. The stability of the porphyrin metallocomplexes depends largely on such factors as the size and formal charge of the complexing metal atom [2].

Many synthetic metalloporphyrins can produce nanosized objects with interesting optical and electronic properties that can be applied in biochemistry, electronics, photonics, and so on. They can form such nanostructures as fibers and thin bands on surfaces. Nanoparticles and sheets are, however, more typical forms [3–5].

Of considerable interest is the possibility of porphyrin derivatives aggregating to form stacks and columns in which the porphyrin heterocycles are arranged parallel or almost parallel to one another. The authors of [6, 7] tried assembling such nanostructures in several steps. They were able to obtain stacks containing up to 15 plates of supramolecules with nine porphyrin cycles in each. It is possible to obtain porphyrin chains by using bridge bidentant ligands [8] and stable sandwich-type structures of complexes of porphyrin and phtalocyanine with rare-earth metals [9, 10]. It is noteworthy that the stability of such structures depends on the geometrical factors of the metal coordinated by the nitrogen atoms.

In spite of the large number of works devoted to porphyrin metallocomplexes and its functional assembling, sandwich-type structures of metalloporphyrins are rarely encountered in them. Studies of their properties and the possibilities of aggregating similar porphyrin polymers are of considerable interest [9, 10]. In this work, the possibility of forming stable sandwich metalloporphyrin structures is examined: we calculate their electronic structure and determine electrical conducting properties.

EXPERIMENTAL

Our calculations were performed in the context of a density functional theory (DFT) [11] with the general gradient adjustment (GGA) of the exchange–correlation potential found in the VASP software. This
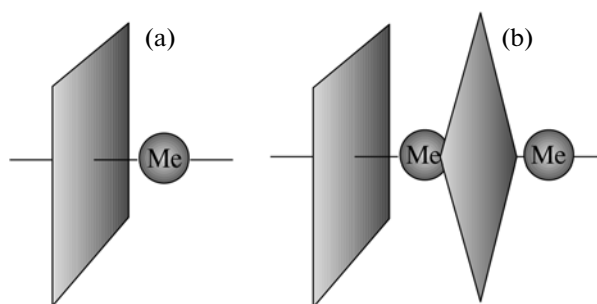
Fig. 1. Elementary cell of a polymer sandwich MeP complexes. (a) Shielded conformation, (b) retarded conformation.

allowed us to perform calculations with respect to periodic conditions [12–14]. The ultrasoft Wanderbild pseudopotential was used in carrying out our work. The cutting energy of the plane waves was 348 eV.

Polymeric sandwich structures, which can be visualized as alternating sequences of porphyrin molecules arranged in parallel and along a z axis, were chosen as the objects of our investigation. Isolated metal atoms are aligned between these molecules on a selected axis that passes through the centers of microcycles perpendicular to their planes. In this case, periodic conditions were used along the z direction. Along the x and y directions, a vacuum interval (10 Å) was used to prevent samples of monomers from neighboring cells from affecting one another. The vector of the reciprocal surface lattice of the first Brillouin zone along the periodical direction was divided into $10k$ points.

We also considered the possibility of various conformational packings of the porphyrin cycles. In one case, all of the monomers were arranged equally relative to one another in each layer (a shielded conformer). The elementary cell of the given polymer contained one porphyrin molecule and one metal atom. In another case, each subsequent monomer was swung 45° relative to the preceding one (a retarded conformer). The elementary cell of a similar con-

former contained two microcycles and two metal atoms (Fig. 1). The optimum lengths of the translation vector along periodic direction z and the equilibrium geometry were calculated for each structure. The potential barrier to a shielded conformer transitioning into a retarded conformer was found for the two most characteristic complexes.

RESULTS AND DISCUSSION

We began by selecting the metal atoms for which it is was possible to assemble stable stack structures with porphyrin. The following elements were considered: Mg, Ca, Sr, Ba, Sc, Y, Ti, Zr, Fe, Co, Ni, Cu, and Zn. We calculated the bond energy between layers in the periodic structure for all stacks of Me-porphyrins:

$$E_{\mathrm{b}} = E_{\mathrm{s}} - E_{\mathrm{mol}},$$

where E_{b} is the bond energy between layers in the periodic structure, E_{s} is the energy found in an individual layer of the sandwich structure, and E_{mol} is the energy of an individual MeP molecule. The negative values of E_{b} point to the energy advantage of forming a periodic structure relative to an individual metal−porphyrin cycle. Stacks with metals having large atom radii like Ba, Sr, Sc, Y, and Zr are stable structures that correspond to the calculated bond energy. The obtained values for the bond energies and equilibrium vectors of translation along the z direction are presented in table.

According to our results, the retarded conformation is preferable for the structures with Zr and Y atoms, while the shielded structure is more advantageous for the structures with Sr, Ba, and Sc. For compounds with scandium, optimization resulted in different distances between alternating layers, and the structure was less advantageous at equal distances. This is likely a manifestation of the Jahn−Teller effect associated with eliminating the degeneracy of an electronic system by reduction its structural symmetry. This phenomenon was discovered during calculations for a unit cell containing a double amount of monomers. No situation of this type is observed in any other case except for ScP complex.

The least difference in bond energies between conformers is seen in BaP and the greatest in ZrP (table). The barriers to a transition from a shielded conformer to a retarded one were calculated; for BaP, the figure is 0.162 eV. This shows the possibility of rapid regroupings of the corresponding conformers. There is no potential barrier to transitions for ZrP and, since the difference between the energies of the conformers is substantial (~0.825 eV), it is likely that only the retarded form can be observed for this complex.

The zone structure and total state densities for describing the electron properties of the investigated MeP are shown in Fig. 2. SrP and BaP stacks are semiconductors, while the structures with a shielded conformation are nondirect gap semiconductors (Fig. 2a) and those with a retarded conformation are direct gap

Equilibrium vectors of translation and bond energies between layers of one-dimentional periodic MeP structures

MeP	Translation vector at z, Å		Bond energy, eV	
	shielded conformer	retarded conformer	shielded conformer	retarded conformer
SrP	3.731	7.341	−1.822	−1.646
BaP	4.081	7.946	−1.657	−1.641
ScP	6.590*	6.399	−0.444	−0.390
YP	3.450	6.662	−1.456	−1.753
ZrP	3.189	6.173	−0.587	−1.412

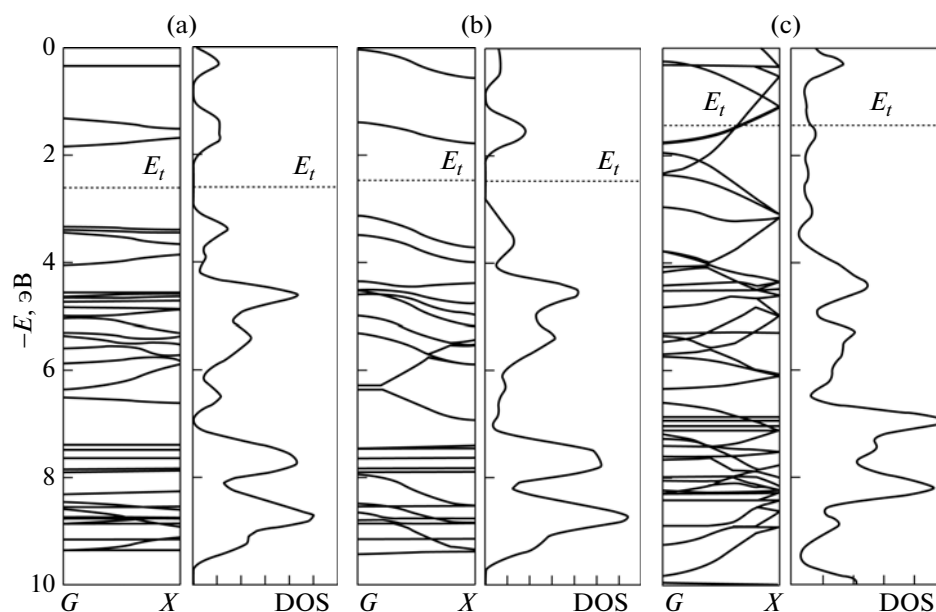* Translation vector for a cell containing a double number of monomers.

Fig. 2. Zone structure and total state densities of polymer sandwich MeP complexes. (a) Retarded BaP conformer, (b) shielded BaP conformer, and (c) retarded ZrP conformer.

semiconductors (Fig. 2b). ScP, YP, and ZrP stacks (Fig. 2c) are semiconductors regardless of the type of conformer.

CONCLUSIONS

The possibility of assembling stack-type metalloporphyrins with different conformations was thus evaluated. Stable structures were shown to form when the metal atoms are Ba, Sr, Sc, Y, and Zr. Retarded conformation is preferable for compounds with Zr and Y, while a shielded structure is most advantageous for compounds containing Sr, Ba, and Sc. Mg, Ca, Ti, Fe, Co, Ni, Cu, and Zn do not form stable stack-type metalloporphyrin complexes.

Of the stable compounds we obtained, only those containing Sc, Y, and Zr were electrical conductors, while complexes with Sr and Ba were semiconductors. The conformation of the latter affects the form of the forbidden gap. These properties allow us to consider the use of similar metalloporphyrins as materials for nanoelectronics to be promising.

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