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Theoretical and Experimental analysis of ZnPc for its local ordering and electronic structure

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ABSTRACT Zinc Phthalocyanine (ZnPc) has been investigated intensely for fabricating plastic solar cells, and there are very limited reports available relating molecular structure and its corresponding macroscopic properties linked with simulation and electronic structure. In fact, our previous reports have demonstrated a partial ordering of the ZnPc molecules [1]. As a continuation of our previous work, we report here the structural determination of atomic and electronic distribution in this material, and a detailed analysis of its involvement in interactions that produce local domains in partial periodic structures. The use of high resolution transmission electron microscopy (HRTEM) and digital processing based on the frequency selection allowed us to distinguish the contrast from local arrays of fringes with distances around 0.37 and 0.35 nm between them. From the quantum mechanical calculations and approximations for single molecules and from classical molecular mechanics for two to six molecule arrays, we identified the type of ordering and the effects on the corresponding frontier orbital (HOMO and LUMO) and the electrostatic potential. The calculated models and a simulation of the HRTEM images demonstrate that the molecular arrays observed in the samples are determined by the electrostatic interactions and the production of arrays influence significantly the optical and electronic properties of the ZnPc material.

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1 Introduction

The search of materials for optical devices, particularly for fabricating cheap solar cells has involved multiple efforts as in the case of synthesis of new materials. During the last few decades, the development of materials involved not only in the experimental methods, but also the theoretical approaches in order to understand the structure and the effects on the general properties in order that they complement each other. Zinc phthalocyanine (ZnPc) has been identified as an excellent candidate because of its flexibility in varying electrical and optical behavior and its own benefit as an organic semiconductors [1–4]. In our previous work [1],

we have reported the synthesis and basic characterization, where we observed a partial periodicity of the material. In the present work, we have utilized the experimental and theoretical methods together in order to understand the possible arrays formation and the corresponding interactions that produce them. The application of high resolution transmission electron microscopy (HRTEM) is considered to be an excellent tools for the study of crystals [5, 6] and small ordered materials [7]. HRTEM analysis along with digital processing and molecular simulation have proved to be a great combination in order to understand the local atomistic orderings as in the case of nanoparticles [8–10], crystalline polymers [11], or even local effects in amorphous materials [12]. HRTEM image simulations have opened the possibility for comparing directly the structural evaluation and distance measurements that are associated to the planes and molecular interaction, and also with the electronic structure that induce arrays and the theoretical models to the experimental data [13]. In this work, both molecular mechanics and quantum mechanics methods are used to study the types of arrays that are formed in the ZnPc molecules. This has also an added advantage of determining the effects in the optical and electronic properties induced from the different configurations modeled. This study also involves the simulation of HRTEM images in order to compare them with experimental data, and to corroborate the theoretical results and to improve our interpretation about the structure of the material and about the electronic properties of this material that can facilitate future material design.

2 Methodology

2.1 Experimental

ZincPhthalocyanine (ZnPc) in bulk form was purchased from Fluka chemie (98% purity and chemical formula is $C_{32}H_{16}N_8Zn$) and thin films of ZnPc were formed by flash evaporation technique under a pressure of 10^{-6} Torr on to well-cleaned glass substrates. The detailed deposition technique is given elsewhere [1]. Microstructural analysis was performed in a HRTEM microscope JEOL 2010FEG, with spherical aberration $C_s = 0.5$ mm and ultimate resolution of 1.9 Å. Before the analysis, the ZnPc powders stripped from the substrate were ground in an agate mortar and dispersed in ethyl alcohol by sonic bath. A drop of this suspension was deposited on a 300 mesh carbon coated Cu grid. The images

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were digitalized in-situ using the Gatan camera in the microscope, and a digital processing was used in the Fourier space in order to enhance the structure of the observed individual reflections.

2.2 Theoretical

The original structure of the Zinc phthalocyanine (ZnPc) has been modeled taking in to account the D_{4h} geometry used in previous experimental and theoretical works [14, 15]. Full geometrical optimization of the molecule by means of a Density Functional Theory (DFT) [16] calculation was carried out using the Becke's three-parameter hybrid function incorporating the Lee, Yang, and Parr (B3LYP) [17] method and the 6-31G* basis set was employed. The minimum energy was confirmed by the frequency analysis. The study of the electronic and optical properties (single point calculation) were performed with the Modified Neglect of Diatomic Overlap/d (MNDO/d) [18] and the Zero Intermediate Neglect of Differential Overlap/S (ZINDO/S) [19] methods. A Single Configuration Interaction (SCI) [20] was also included in the simulation of the spectra. The SCI calculations were limited to the eight highest occupied and to the eight lowest unoccupied molecular orbitals. Geometries of the ordered systems (from two to six molecules of ZnPc) were obtained by Molecular mechanics, with specific MM+ [21] optimization, and calculating the corresponding single point by the DFT method in order to evaluate the relative energy states. The map of the frontier orbital contours (HOMO and LUMO) and electrostatic potential were performed from a "single point" AM1 [22] calculation using an optimized geometry (MM+ or B3LYP/6-31G* depending on the case). We used the SimulaTEM program [23] that is based on the multislice method, and finally the models were used to simulate the corresponding HRTEM images under the same conditions of the experimental environment.

3 Results and discussion

The thin films of ZnPc samples have been reported as good candidates for solar cell devices because of their optical properties; however, the internal structure or even the source for the periodic patterns reported by various authors have not been fully understood. In our case, we have identified multiple peaks from the X-ray diffraction pattern (Fig. 1a), which denotes low intensity measurements, but with well defined angles and consequently diffraction distances. As an example, the peak numbered 6 corresponds to 0.3707 nm interplanar distance. In order to understand the source of this signal, the use of HRTEM images was improved further, obtaining information about the local domains with a defined order and periodicity mainly along the thin borders of the sample, as shown in Fig. 1b, and the amplification of that zone (Fig. 1c), where fringe contrast can be associated to the local periodicity with a d spacing almost close to the value obtained from the X-ray pattern.

In the Fig. 2, another example of this ordering effect is observed, the contrast of small ordered lines appears again in the image and the measurement in the selected area (Fig. 2b) corresponds directly to the distance of 0.3512 nm. In the Fast Fourier Transform (FFT) (Fig. 2c), three different zones of

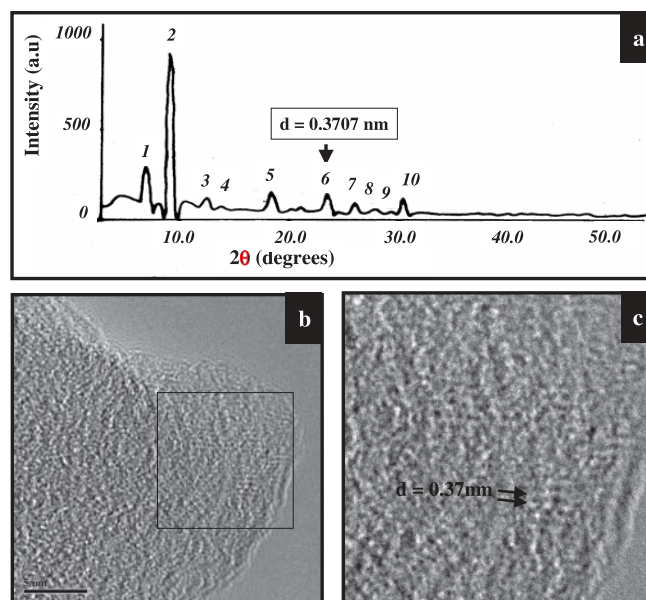


FIGURE 1 Analysis of periodicity in ZnPc samples. **a** X-ray diffraction pattern and **b** HRTEM image with its **c** local magnification that denotes an interplanar distance of 0.37 nm between ordered fringes

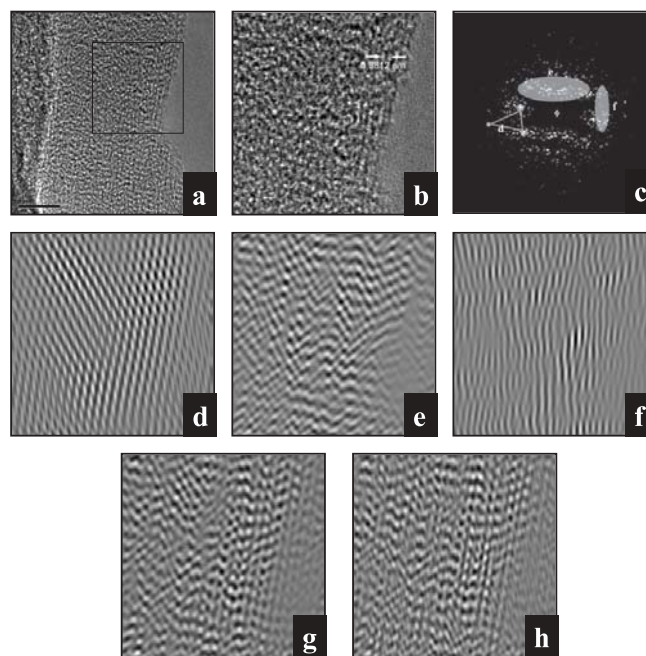


FIGURE 2 HRTEM analysis of a ZnPc sample. **a** Original image, **b** corresponding FFT with three different zones of frequencies to generate the filtered images of (**d**–**f**)

frequencies are selected and marked, which allow us to distinguish the source of this periodicity. The use of digital filtering gives us the images corresponding to each zone marked in the Fig. 2c, where two oval shaped images correspond to Fig. 2e and f while Fig. 2d correspond to the three points observed in the left side of the FFT. In fact, the single frequency sources are observed in Fig. 2d–f, which contributes to the final image (Fig. 2b). It is clear that the three different zones correspond to fringes, and local arrays that are generated by the ZnPc molecule arrangements as observed in the HRTEM images.

By using the information obtained from the HRTEM and processed images, we can observe that the ZnPc thin film samples must be composed of a set of multiple molecules that produce local domains with distances well defined as observed commonly in the crystal structures. However, the composition and type of interaction of ZnPc is poorly understood. The use of molecular simulation becomes quite important to determine how the ZnPc molecules must be ordered and how they produce local arrays based on their real interactions.

Figure 3a shows the atomic and electronic structure of a single ZnPc molecule. The structure evaluated by DFT geometry optimization was used for deriving single point energy by using both MNDO/d and ZINDO/S approaches, which generated the electronic transitions and are in good agreement with the experimental absorption bands (Fig. 3b). The method ZINDO/S agrees more with the experimental spectrum of the Q band (690 nm), which is almost coinciding and better reproduced than the B band at 330 nm. The electrostatic potential was similarly distributed throughout the atomic structure, inducing homogeneous electronic clouds (Fig. 3c). The HOMO and LUMO distributions displays an a_{1u} and e_g symmetry (Fig. 3d and e) corroborating the homogeneity of the electronic structure of the molecule and in good agreement with the experimental and calculated first absorption band (Q) associated to the transition HOMO–LUMO ($a_{1u} \rightarrow e_g^*$) as reported earlier by Edwards and Gouterman [24].

The above calculations allow us to understand the single molecule properties, but it is necessary to calculate the two molecule configuration to identify the main parameters for the possible ordering of ZnPc molecules, as in the Fig. 4 where a two molecules study is shown. The multiple molecules are normally evaluated by classical molecular mechanics (MM+//B3LYP/6-31G*), and the types of inter-

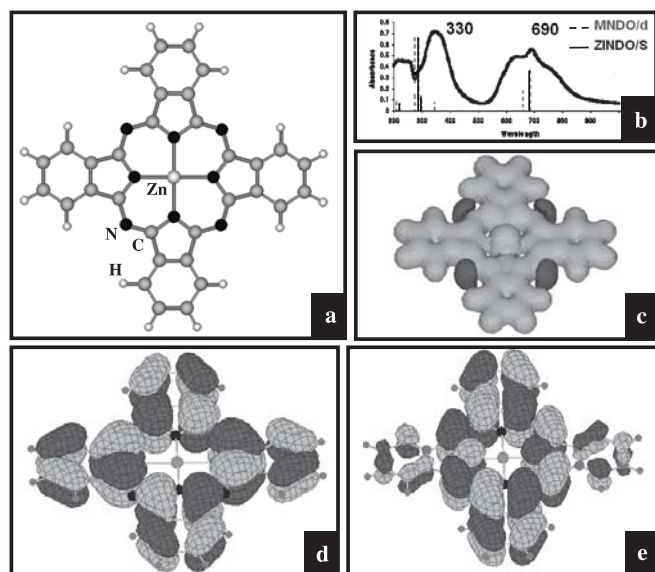


FIGURE 3 a Optimized geometry (B3LYP/6-31G**) of a ZnPc molecule, with its corresponding b calculated transitions with MNDO/d and ZINDO/S (dotted line) to be compared to the absorption spectra of a typical flash-evaporated ZnPc thin film. And c electrostatic potential, d HOMO and e LUMO obtained from a “single point” AM1 calculation using the DFT optimized geometry

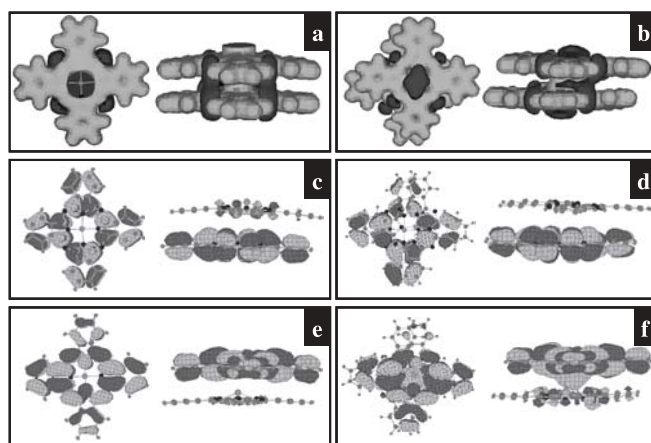


FIGURE 4 Optimized geometry (MM+) of two ZnPc molecules showing the electrostatic potential iso-surface, and HOMO and LUMO contours for a Zn–Zn aligned (a, c and e) and Zn–Zn no aligned (b, d and f). Perpendicular and parallel views (left and right respectively) are shown for a better understanding

actions can be studied even though in single molecule planar configuration the results used are a little distorted as has been reported previously [25], which are not produced by the molecular interaction. These calculations based on an all atomic force-field have produced good results for large number of atoms when it is fixed to the semi empiric parameters with no bonding effects.

Among the various calculations performed for the evaluation of stable state (obtained as low energy), two main configurations were selected and shown in the Fig. 4. One of them shows the two Zn atoms aligned in the middle (Zn-A) (Fig. 4a), while the second one has slight misaligned rings (Zn-nA) (Fig. 4b) where the perpendicular and parallel orientations are shown for clarity. In the Fig. 4, the electrostatic potential iso-surface and frontier molecular orbital (AM1) distributions are also shown for both configurations. It can be observed that there is high homogeneity in the first case, where the electrostatic potential is observed with great symmetry, which permits us to observe the interaction between the molecules as a continuation of the same atom (Fig. 4a). The HOMO (Fig. 4c and d) and LUMO (Fig. 4e and f) distributions are too similar to that obtained for the single molecule model, but presenting a polarization in the sites, because the HOMO is mainly located in the bottom molecule and the LUMO in the opposite side. This behavior changes when the molecules are not aligned, where the electrostatic potential is elongated to the displacement direction, which is clear in the parallel view (Fig. 4b). In the HOMO (Fig. 4d) and LUMO (Fig. 4f), we can also observe a zone with no orbital on one of the rings and a neck between the Zn atoms for the LUMO. This orbital condition influences a high interaction and a simple way to donate and accept electrons, which makes favorable the formation of molecular arrays, sharing clouds and producing hard symmetry and preferential coordination sites. It must be noted that the most stable configuration corresponds to the non aligned molecules; however, the small difference of energies determines a coexistence of them.

The effect of the electronic structure is directly related with the local charge of the molecules and its corresponding

Mulliken charge	1 Molecule	2 Molecules (Zn-A)		2 Molecules (Zn-nA)	
		Ring A	Ring B	Ring A	Ring B
Zn	+0.998	+1.018	+1.052	+0.925	+0.943
N1	−0.791	−0.871	−0.893	−0.684	−0.735
N2	−0.665	−0.668	−0.656	−0.628	−0.623
C1	+0.604	+0.633	+0.638	+0.488	+0.515
C2	−0.015	−0.006	+0.002	−0.005	+0.012
C3	−0.002	−0.001	−0.001	+0.008	−0.002
C4	+0.018	+0.006	+0.015	+0.042	+0.022

TABLE 1 Mulliken charges for 1 Molecule and 2 Molecules both Zn–Zn aligned and no aligned of ZnPc

deformations. In Table 1, the Mulliken atomic charges for the constitutive elements of the molecules are shown. From the charge values, it is possible to observe that when the Zn atoms are aligned, the charge increases because of the double contribution, and due to the external atoms the charge reduces

because of stronger boundary effects. However the charges of both molecules are quite similar and homogeneous. When the molecules are not aligned, the charge of Zn is reduced because of the polarization behavior. Similar behavior is also observed for nitrogen and carbon atoms (see Fig. 3a for various N and C). Besides the charge reduction, the variation of charge between Zn-nA and Zn-A demonstrates an effect of attraction and electron sharing, which is reduced when the alignment is changed. This must be because of the boundary effect that should be balanced by the neighboring atoms which implicit a search for an order and to form arrays with equilibrated electronic structure.

We can determine the influence of charges in the formation of parallel arrays; however, the effect of this in the HOMO–LUMO gap must be considered because the main application of this material is its use in solar cells as well as in optical devices. In Table 2, the HOMO–LUMO gap and total energy are shown for the single molecule, and both two molecules

Model	HOMO (eV)	LUMO (eV)	Gap (eV)	Total energy (eV)
1 Molecule	−5.1727	−2.8336	2.3391	−93 304.5923
2 Molecules (Zn-A)	−4.6137	−2.6678	1.9459	−186 598.3846
2 Molecules (Zn-nA)	−4.8170	−2.9459	1.8711	−186 605.6146
2 Molecules (Zn-A) ^a	−4.8094	−2.8153	1.9941	−186 609.2590
2 Molecules (Zn-nA) ^a	−4.8722	−2.7043	2.1679	−186 609.3893

^a The configuration is the same but the geometry of each ZnPc molecules is based in the B3LYP/6-31G** calculation

TABLE 2 Single point calculated frontier orbitals, gap and total energy for one and two ZnPc molecule configurations

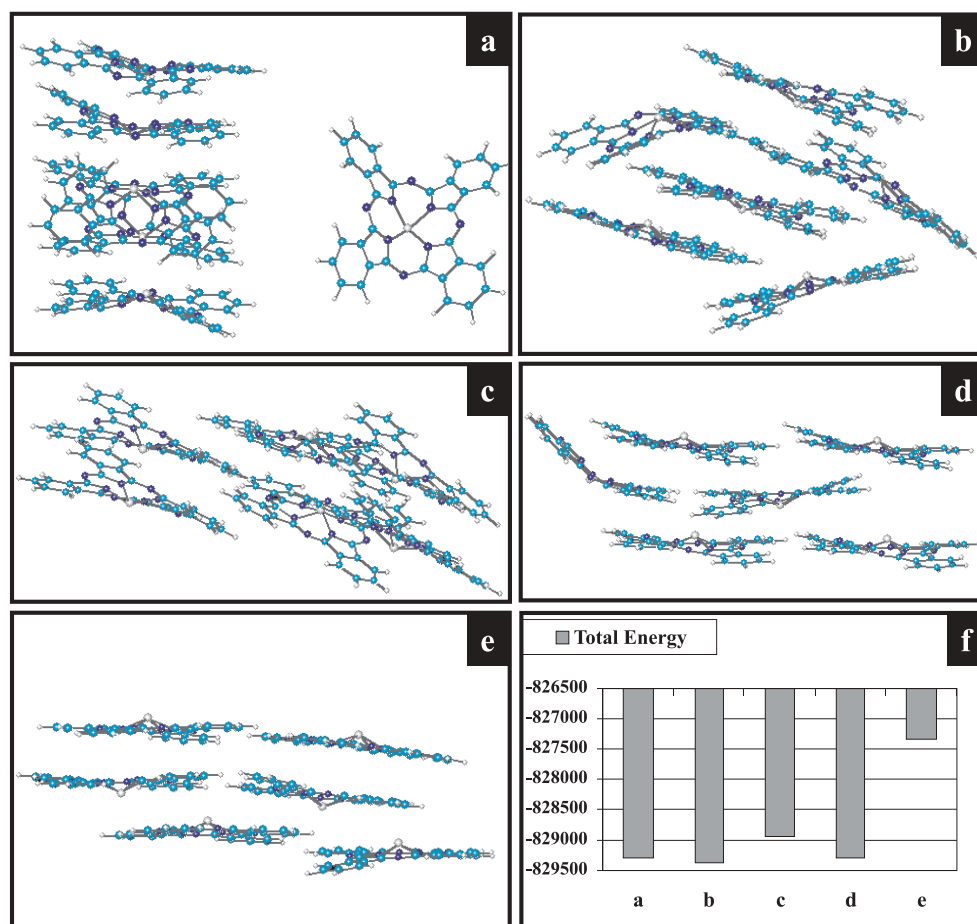


FIGURE 5 Six molecules array configurations of ZnPc calculated by molecular mechanics with the total energy plot

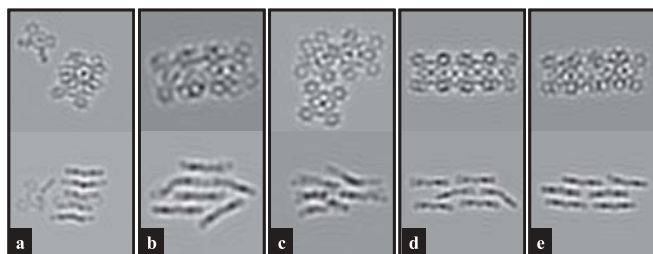


FIGURE 6 HRTEM simulated images for each model of the six molecules arrays. In each case perpendicular and parallel views are shown

configurations. It is clear that, when the HOMO and LUMO values are higher for the nonaligned system, the gap is quite near for both two molecule configurations and the total energy. This allows us to determine that these two configurations must coexist in the samples, and their effects on the optical properties are similar, and it cannot be recognized directly the effects of one or the other configurations. In the Table 2, configurations of arrays based on molecular mechanics are considered. However, we have also used the mixed method of the molecule array including the DFT based configuration in order to improve the energy evaluations, which shows a better matching to the experimental values [1] (marked with “).

In fact, the boundary effects become important, because this material is not an infinitum growing array as is the case of crystals; but the behavior can be observed considering a larger number of molecules in order to determine the interaction of neighboring atoms. In this way, molecular mechanics optimization was used for calculating the most stable array. Figure 5 shows five different configurations obtained by molecular mechanics geometry optimization and single point energy calculation (MM+//AM1). These configurations were determined as the most stable types and the energy for each structure is shown in the plot (Fig. 5f) included in the figure. While the first configuration includes molecules that are perpendicular (Fig. 5a), and the others show minimal differences, which present almost parallel arrays with curvatures induced by the boundary of arrays. This behavior is quite interesting because even when there is a curvature, the intermolecular distances match with the measured ones (0.371 and 0.352 nm) of the experimental data. From these configurations the less stable one is the array of parallel molecules, which has significantly higher energy than others. This consideration allows us to determine the boundary effect in the material, which is commonly the main factor for distortion of materials. However in the ZnPc samples, this creates a condition for the generation of small periodic domains with finite size.

The energy plot (Fig. 5f) shows a preference for producing curved arrays. Also the first model demonstrates that the kind of interaction between parallel molecules and perpendicular ones produce stable configurations. Besides the theoretical interpretation, we used the models to simulate the HRTEM contrast that they would produce. In Fig. 6, the corresponding HRTEM simulated images are shown in order to identify the effects of the arrays in the electron scattering and on the produced contrast for the same models (Fig. 5).

In the Fig. 6, two views are shown for each model; a perpendicular flattest of the molecules and a parallel to them. In the perpendicular images, the rings can be identified. How-

ever, it is clear that there is no periodicity as observed in real crystal images and this contrast would be lost when there are several molecules, and also when they are deposited on a grid for the observation. The contrasts of parallel views of the different models demonstrate the kind of periodicity that must generate the diffraction evidences in the experimental results. A simple comparison allows many similar details in the simulated images and the experimental ones to be identified.

In fact, the obtained contrast is recognized in the experimental images, but after the digital processing with help of the frequencies mask, since the extra contribution of the substrate and the thickness of the samples uses to reduce the evidences of the contrast in the HRTEM images.

4 Conclusions

The structural analysis and HRTEM images, along with simulation, support the formation of molecular arrays with the electronic structure fixing the molecular spacing and producing mainly parallel arrays in small domains. These arrays produce the frontier orbital gap that matches the experimental values, and also the experimental data of periodicity, which could also be reproduced theoretically. The theoretical calculations supported the existence of molecular arrays, and this kind of ordering helps electronic and photonic device applications. Also, the quantum mechanical calculations determine the basis for the material properties. In this case, we used classical molecular mechanics for models with a larger number of molecules and quantum approaches for the small number of atoms along with geometry optimization that corresponds to a common method for improving the atomic and electronic structural study. We report in this paper on a complementary methodology for the study of molecular arrays with a high success rate for reproducing and supporting experimental data. Geometry optimization, single point energy and HRTEM image simulation together represent an effective method for the understanding of material structure. However, a full characterization and the experimental HRTEM processing is needed, which allows for identifying patterns and parameters to a real extent. This opens the expectative for structure modifications searching for specific properties based on the atomic and electronic configurations, used in designing the material with fundamental knowledge in all the scales of the material.

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