PHYSICAL REVIEW B **85**, 035423 (2012)

Large organic molecule chemisorption on the SiC(0001) surface

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(Received 4 May 2011; revised manuscript received 24 October 2011; published 17 January 2012)

We present a density-functional theory (DFT) study combined with scanning tunneling microscopy (STM) experiments of the chemisorption of the N,N'-bis(1-hexylheptyl)perylene-3,4:9,10-bis(dicarboximide) molecule, noted here as DHH-PTCDI, on the SiC(0001)-3 × 3 surface. Five possible adsorption configurations have been investigated in which molecular adsorption occurs on two adjacent Si adatoms via different pairs of atoms of the molecule. We have calculated the energies, structures, density of states, local density of states, and a calculated STM image and show that chemisorption via two oxygen atoms located on the *same side* of the molecule on two adjacent Si adatoms is the most favorable, in agreement with the experimental STM images. A comparison between the PTCDI and the adsorption of another large organic molecule (phthalocyanine) on the SiC(0001) surface completes this work.

DOI: 10.1103/PhysRevB.85.035423 PACS number(s): 68.43.Bc, 73.20.Hb, 68.47.Fg, 68.37.Ef

I. INTRODUCTION

The interaction of organic molecules with semiconducting surfaces is a potentially important aspect in the future development of nanotechnology. New types of organic-inorganic interfaces can be envisaged which open exciting possibilities of controlling surface properties. In particular, organic functionalization is becoming an important tool for the expansion of semiconductor-based devices. These techniques may be used, for instance, to integrate molecular functionality into inorganic components. The main applications concern molecular electronics,[1–3] nanocatalysis, optoelectronics,[2–4] and biosensors.[5–8] In this field, biocompatible semiconductor materials could be the basis for implantable biosensors or other electrical components *in vivo*.

Due to its biocompatibility, transparency, and outstanding mechanical properties, silicon carbide (SiC) is a promising candidate for such applications. However, finding suitable molecules involving the appropriate chemical group susceptible to act as an anchor on SiC is difficult and, until now, only a few studies have investigated SiC functionalization. By means of *ab initio* calculations, Cicero *et al.*[9] studied the adsorption of CH_3X-like organic molecules on the cubic SiC(001). The adsorption of small nitrogen-containing species onto the Si and C surfaces of SiC(0001) was theoretically investigated using density-functional theory (DFT) by Olander *et al.*[10] Pyrrole functionalization on SiC was also investigated and it was shown that the bonding of the molecule on the 3 × 3 hexagonal SiC reconstruction through the dissociation of a N-H bond is favorable.[11] More recently, combined STM and DFT studies have probed the interaction of phthalocyanine molecules (H_2Pc) with a SiC(0001)-3 × 3 surface. H_2Pc molecules were found to chemisorb through a cycloaddition reaction of two conjugated imide groups with two silicon adatoms. This type of anchoring opens numerous perspectives for the organic functionalization of a biocompatible wide band-gap semiconductor.[12,13]

Another potentially interesting molecule for the SiC functionalization is the N,N'-bis(1-hexylheptyl)perylene-3,4:9,10-bis(dicarboximide) molecule, noted here as DHH-PTCDI. Indeed, when this molecule is adsorbed on the SiC(0001)-3 × 3 surface, both the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) located within the SiC band gap are electronically decoupled from the substrate.[14] Given the optical properties of the clean surface,[15] molecular luminescence is expected even at room temperature. This recent scanning tunneling microscopy (STM) study[14] of the DHH-PTCDI/SiC(0001)-3 × 3 system revealed the existence of two different adsorption configurations. Figure 1 shows filled-state STM images (sample bias −2.0 V and −3.0 V, tunnel current 0.3 nA) of the DHH-PTCDI molecules adsorbed on the 3 × 3 reconstructed SiC(0001) surface where they are seen as double protrusions. There are three equivalent orientations of the molecule with respect to the surface imposed by the threefold symmetry of the adatoms on the SiC surface. A close-up of the most common configuration (80%) in Fig. 1(b) reveals that the long axis of the molecule is slightly offset with respect to the Si adatoms, while Fig. 1(c) shows a second less frequently observed configuration (20%) where both the long and short axes of the molecule are slightly offset with respect to the Si adatoms.

In this paper, we propose a structural and electronic study of the PTCDI molecule interaction with the SiC(0001)-3 × 3 surface, in the framework of DFT calculations. Our calculation method and models used to simulate the molecule and substrate are described in Sec. II along with a description of the experimental procedure. We then present our results of the energetic, structural, density of states (DOS), and local density of states (LDOS) studies and calculated STM image, as well as a comparison with the experimental data in Secs. III–VI.

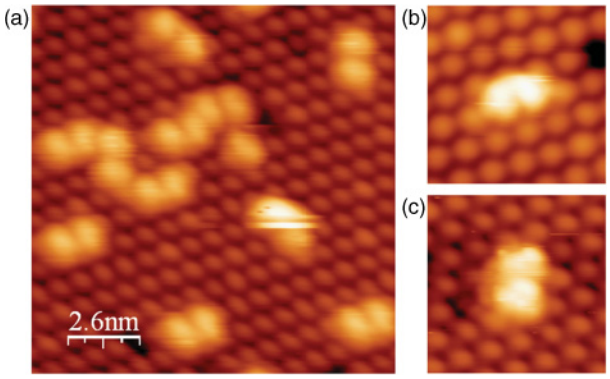

FIG. 1. (Color online) (a) STM image of DHH-PTCDI molecules adsorbed on the SiC(0001)-3 × 3 surface (image size 21 × 21 nm; tunneling conditions −2.0 V and 0.3 nA). [(b),(c)] Images showing close-ups of two single molecules and their position with respect to the surface adatoms (image size 5 × 5 nm; tunneling conditions −3.0 V and 0.3 nA).

A comparison between the adsorption of two large organic molecules (H_2Pc and PTCDI) on the SiC(0001)-3 × 3 surface and related conclusions completes this work.

II. METHOD

We performed DFT calculations by using the VASP code[16–18] in generalized gradient approximations (GGAs) with PW91 functionals[19] and Projector Augmented Waves (PAW) pseudopotentials.[20] The Brillouin zone was sampled using a single k point at the Γ point, which is a reasonable choice given the large size of the chosen supercell.

The Si-rich 3 × 3 reconstruction exhibits dangling bonds (DBs) located on the top of pyramidal Si structures separated by about 9.3 Å from each other.[21,22] The periodic slab contains six layers (three layers for the reconstruction, one bilayer of SiC, and one layer of hydrogen atoms). The H atoms were added on the back side to saturate the DBs (Fig. 2).

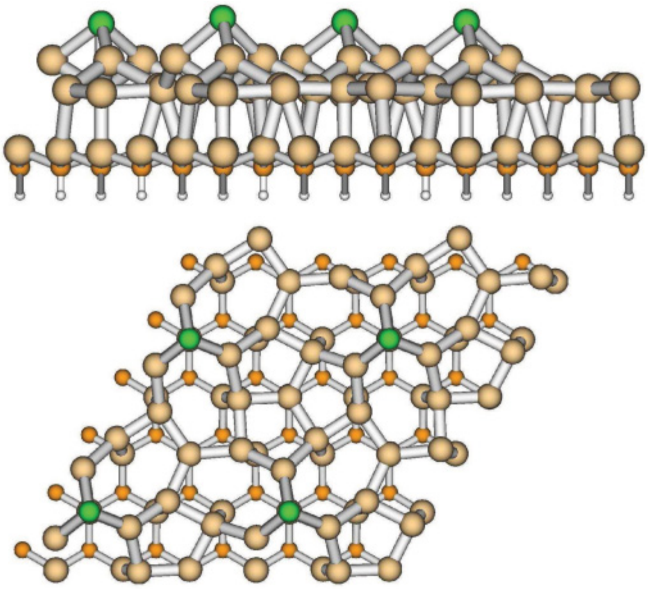

FIG. 2. (Color online) Top and side view of the SiC(0001)-3 × 3 surface unit cell used in the DFT calculations. The Si adatoms, other silicon, carbon, and hydrogen atoms are designated by green, yellow, orange, and white circles, respectively.

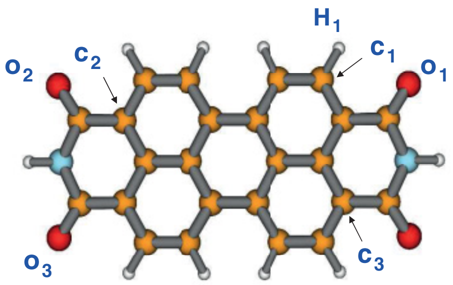

FIG. 3. (Color online) Schematic model for an isolated PTCDI molecule. The oxygen, carbon, nitrogen, and hydrogen atoms are designated by red, orange, blue, and white circles, respectively.

The vacuum region between slabs along the z direction (normal to the surface) is 12 Å. The top four layers and the whole molecule were allowed to relax. The energy of the system was considered to be minimized when the residual forces on the atoms were less than 0.04 eV/Å. The model for an isolated PTCDI molecule is shown in Fig. 3. The notations DHH-PTCDI and PTCDI are used to distinguish, respectively, between the complete N,N'-bis(1-hexylheptyl)perylene-3,4:9,10-bis(dicarboximide) molecule with alkyl chains and a simpler molecule without the alkyl chains used in our calculations. The complete system involves 200 atoms. The adsorption energy of a given configuration (substrate + PTCDI) was defined as the total energy of this configuration minus that of the isolated PTCDI molecule and that of the clean SiC surface. Local density of states calculations, using the Tersoff-Hamann approximation,[23] were performed for comparison with the STM images. The STM image was calculated (using a tungsten tip) by feeding the atom positions from the VASP code into the BSKAN code,[24] which was designed to describe electron transport through a vacuum barrier. The theoretical model is based on multiple-scattering theory.[25]

In order to estimate whether the energy difference in the adsorption probability for the investigated models is significant, we also considered a larger slab involving 10 layers. The complete system involves 344 atoms in this case. The same ordering in the adsorption energies was observed and the relative adsorption energy variation was less than 0.1 eV. We therefore considered a six-layer slab for the electronic structure study.

The STM experiments were performed in ultrahigh vacuum at room temperature (base pressure 3×10^{-11} Torr) using electrochemically etched tungsten tips. A highly nitrogen-doped (density 3×10^{18} cm^{-3}) n-type 6H-SiC(0001) single-crystal wafer was used. After outgassing, the SiC sample was flashed at 1100 °C to remove the native oxide, followed by silicon deposition on the surface at 650 °C for a few minutes,[26] giving a well-reconstructed 3 × 3 surface.[14] The N,N'-bis(1-hexylheptyl)perylene-3,4:9,10-bis(dicarboximide) DHH-PTCDI was synthesized by reaction of perylene-3,4,9,10-tetracarboxylic dianhydride with 1-hexylheptylamine, prepared from 7-tridecanone.[27] Double-pass chromatography (chloroform/SiO_2) was used for final purification. The DHH-PTCDI molecules were evaporated on the clean SiC(0001)-3 × 3 surface using a Knudsen cell at 200 °C placed 4 cm in front of the sample. The exposure time was 30 s.

III. ENERGETIC STUDY OF THE PTCDI/SiC(0001)-3 × 3 SYSTEM

Five possible adsorption configurations of the PTCDI molecule on the SiC(0001)-3 × 3 surface have been investigated. These five models are shown in Fig. 4 using the atomic notations indicated in Fig. 3. Model M1: adsorption via two oxygen atoms, O_1 and O_2, localized on the *same side* of the molecule on two adjacent Si adatoms; model M2: adsorption via two oxygen atoms, O_1 and O_3, localized on *opposite sides* of the molecule on two adjacent Si adatoms; model M3: adsorption via two carbon atoms, C_3 and C_2, localized on opposite sides of the molecule on two adjacent Si adatoms; model M4: adsorption via one carbon atom, C_1, and one oxygen atom, O_2, on two adjacent Si adatoms *without dissociation*; and model M5: adsorption via one carbon atom, C_1, and one oxygen atom, O_2, on two adjacent Si adatoms *with dissociation* of the molecule.

We investigate, in a first step, the adsorption energies by using a six-layer slab. With an adsorption energy, E_{ads} (M1) = −2.36 eV, model M1 is found to be the most likely one. Models M5, M2, M4, and M3 are disfavored with respect to model M1 by 0.01, 0.34, 0.65, and 1.51 eV, respectively.

The adsorption energy difference between models M1 and M5 is small. But, experimentally, dissociated H adsorption can be excluded: H adsorption on a Si adatom would induce a darker Si adatom. Such sites are not observed after adsorption of the DHH-PTCDI molecules as is obvious from the STM images. This observation excludes model M5.

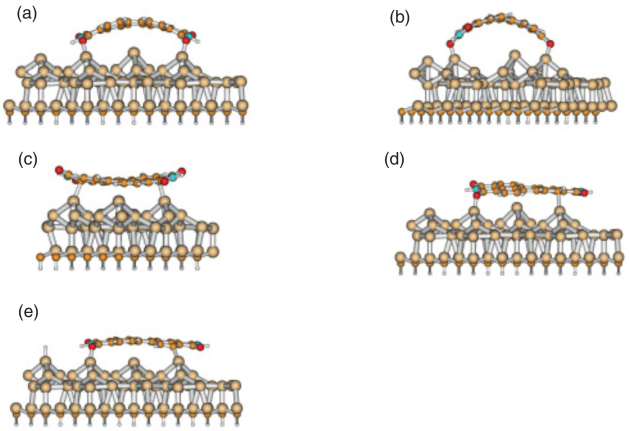

FIG. 4. (Color online) Side views of the optimized configurations of the five models investigated in this work: (a) M1, (b) M2, (c) M3, (d) M4, and (e) M5. The colors used to designate the atoms are the same as in Figs. 2 and 3.

IV. STRUCTURAL CHARACTERISTICS

Side views of optimized configurations of the five models are shown in Fig. 4. A close examination of the structural characteristics of each model presented in Table I will help us to understand these results.

In model M1, the Si-Si distance ($d_{\text{Si}-\text{Si}}$) increases after molecular adsorption, while the O_1-O_2 distance ($d_{O_1-O_2}$) decreases. The difference between $d_{\text{Si}-\text{Si}}$ and $d_{O_1-O_2}$ is reduced. To accommodate the bond formation, the molecule skeleton has to undergo a bending deformation inducing a compressive stress, whereby the central part of the molecule is pushed away from the surface [Fig. 4(a)]. The vertical distance between the Si adatoms and the farthest carbon atoms is 3.46 Å.

If the two oxygen atoms are localized on opposite sides of the molecule (model M2), we notice an analogous behavior as observed in the case of model M1, in that the molecule is distorted, but the Si-Si and O_1-O_3 distances are not so close after adsorption [Fig. 4(b)]. In particular, the central part of the molecule is forced to move even further away from the surface. The vertical distance between the Si adatoms and the farthest carbon atoms is 4.29 Å. The M2 adsorption energy thus decreases with respect to model M1.

In model M3, $d_{\text{Si}-\text{Si}}$ decreases which is the opposite behavior to that observed in models M1 and M2. In order to reduce the stress, the Si-C distances increase leading to weaker bond strength. The deformation of the central part of the molecule is toward the surface [Fig. 4(c)]. The significant repulsion between the central part of the molecule and the surface increases the adsorption energy with respect to models M1 and M2. Even if the difference between the Si-Si and O-O (models M1 and M2) or C-C (model M3) distances are more

TABLE I. Si-Si, O_1-O_2, O_1-O_3, C_3-O_2, C_1-C_2, Si-C, and Si-O distances (Å) before and after the PTCDI molecule adsorption on the SiC(0001)-3 × 3 surface.

Before adsorption	
SiC substrate	Distance (Å)
$d_{\text{Si}-\text{Si}}$	9.29
PTCDI molecule	
$d_{O_1-O_2}$	11.45
$d_{O_1-O_3}$	12.33
$d_{C_3-O_2}$	8.60
$d_{C_1-C_2}$	7.55

			After adsorption				
Models	$d_{\text{Si}-\text{Si}}$	$d_{O_1-O_2}$	$d_{O_1-O_3}$	$d_{C_3-O_2}$	$d_{C_1-C_2}$	$d_{\text{Si}-\text{C}}$	$d_{\text{Si}-\text{O}}$
M1	9.59	10.31			7.67		1.73 1.73
M2	9.69		10.73				1.73 1.73
M3	8.97			8.67		2.11 2.20	
M4	9.13					2.25	1.73
M5	9.24			8.48		1.90	1.74

important before relaxation, the molecule prefers to bend so that bonding can take place via the oxygen atoms.

Adsorption via atoms C_1 and O_2 (model M4) presents an intermediate case in the sense that the Si-Si and C_1-O_2 distances change very little, being rather favorable before adsorption. We observe only small deformations of the Si-O and Si-C bonds and the adsorbed molecule remains nearly planar. However, this is not sufficient and model M4 remains less favorable than the adsorption via two oxygen atoms, principally because the Si-C bond is less favorable than the Si-O bond in the case of adsorption on hexagonal SiC surfaces.

Model M5 considers a different case involving adsorption via the C_1 and O_2 atoms but with a C-H bond dissociation. The hydrogen atom, noted as H_1 in Fig. 3, adsorbs on a neighboring Si adatom. Here, the Si-C distance is shortened to 1.90 Å instead of 2.25 Å in the undissociated case (M4). The Si-C bond is thus stronger, implying a more favorite adsorption configuration. Moreover, the saturation of a neighboring Si adatom dangling bond by the hydrogen atom resulting from the dissociation of the C-H bond also favors stability.

V. LDOS AND COMPARISON WITH THE STM IMAGES

We continue with our study of the PTCDI molecule chemisorption by investigating the local density of states of the M1, M2, M3, M4, and M5 models integrated over the energy window between E_F and $E_F - 3$ eV. The results are reported in Fig. 5 for comparison with the STM images in Figs. 1(b) and 1(c).

The position of the molecule with respect to the neighboring adatoms and the overall shape of the STM image enable us to distinguish between the different adsorption configurations shown in Fig. 5. By comparing each of the LDOS models with the STM image of Fig. 1(b), it can be seen that model M1 is in the correct position with respect to the neighboring adatoms in contrast to the cases of the other investigated models. (Note that model M5 can be excluded on the grounds that dissociative adsorption is not observed in the experimental STM images, as explained in Sec. III). In order to make a clear comparison with the experimental STM data, we subsequently performed a precise STM image calculation for the M1 model by feeding the atom positions from the VASP code into the BSKAN code.[24,25] The calculated image is shown in Fig. 6 alongside the experimental STM image [from Fig. 1(b)]. The calculated STM image is strikingly similar to the experimental image, clearly showing the presence of two protrusions as observed in the experimental image in Fig. 1(b).

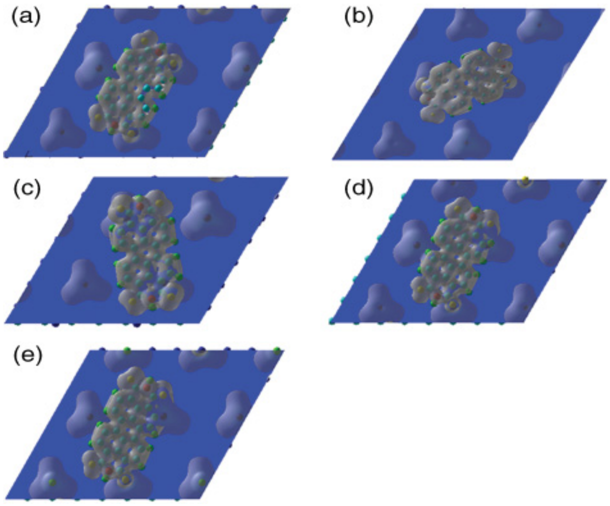

FIG. 5. (Color online) Top view of isodensity maps ($0.008e^-/\text{Å}^3$) of the PTCDI molecule on the SiC(0001)-3 × 3 surface for the five models integrated over the energy window between E_F and $E_F - 3$ eV. Our figures show the molecule and Si adatoms only. (a) M1, (b) M2, (c) M3, (d) M4, and (e) M5.

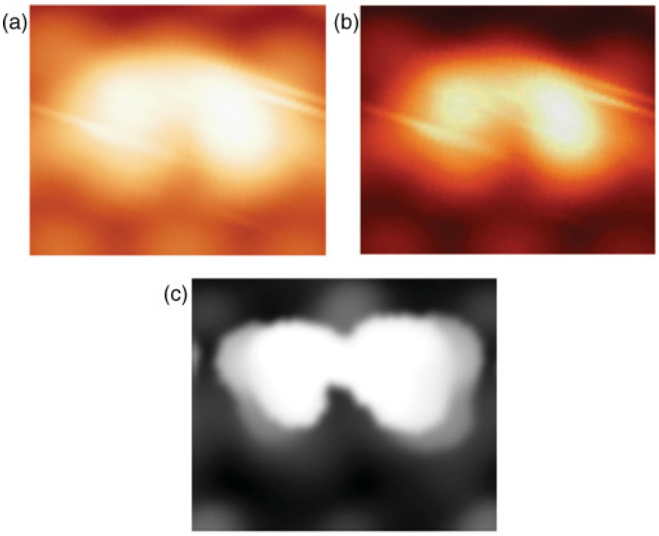

FIG. 6. (Color online) [(a),(b)] Experimental images of the PTCDI molecule. The nonlinear color code has been used in (b) to accentuate internal molecular features. The experimental image has been rotated with respect to that shown in Fig. 1(b) (image size 5 × 5 nm; tunneling conditions −3.0 V and 0.3 nA). (c) Calculated STM image for the M1 model using a tungsten tip (−2.8 V and 0.3 nA theoretical current).

To summarize our energetic, structural, LDOS, calculated STM image studies, the PTCDI molecule adsorption via two oxygen atoms localized on the same side of the molecule on the SiC(0001)-3 × 3 surface (model M1) is the most likely. Let us also notice that the STM experiments, where the image of the molecule shown in Fig. 1(b) is observed in nearly 80% of all cases, also strongly supports model M1 with respect to all the other models investigated. In the next section, we focus only on this model.

VI. DENSITIES OF STATES

The densities of states as a function of energy were investigated for the isolated molecule and the most likely model M1 and are reported in Figs. 7(a) and 7(b). In order to assist our interpretation of the HOMO and LUMO states, the corresponding local densities of states were also calculated (Fig. 8). Concerning the isolated molecule, they were compared to the results of Chiş *et al.*[28] and good agreement was obtained for both the HOMO and the LUMO. Let us first consider the HOMO. Comparing the LDOS of the isolated molecule to those of the chemisorbed molecule, we observe a small deformation of the HOMO on the surface. The overall symmetry of the molecular orbital with respect to the long axis

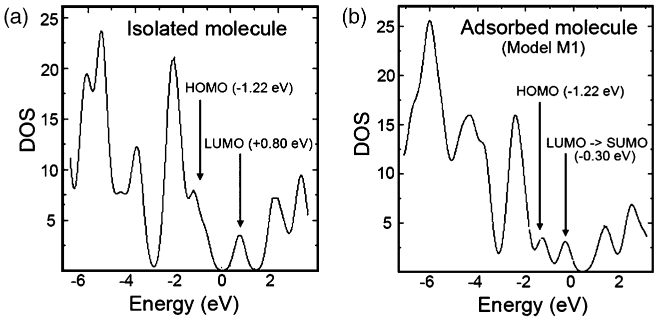

FIG. 7. Calculated density of states (DOS) of the PTCDI molecule showing the HOMO and LUMO states (SOMO in the case of adsorbed molecule). (a) DOS of the isolated molecule and (b) DOS for the adsorbed molecule in the case of model M1.

of the molecule (vertical) is very similar. The main changes concern particularly the region surrounding the O_1 and O_2 atoms, where the molecule is attached. However, the nitrogen levels, which are not present in the isolated molecule, come into play after molecular adsorption by becoming occupied.

Secondly, we observe in the DOS curves that the LUMO is shifted to lower energy to below the Fermi level after molecular adsorption (noted now as SOMO: single occupied molecular orbital). This corresponds to a charge transfer from the SiC substrate to the molecule via the two covalent Si-O bonds.[14] As observed for the HOMO, the orbital symmetry with respect to the long molecular axis is nearly the same after chemisorption. The main changes involve a greatly increased occupation of the nitrogen levels, which are apparently more important in the LUMO density of states than the HOMO.

VII. COMPARISON WITH THE BEHAVIOR OF H_2Pc ON SiC(0001)-3 × 3 AND CONCLUSIONS

To conclude our DFT and STM studies, the most likely chemisorption mechanism for the PTCDI molecule on the SiC(0001)-3 × 3 surface consists in an adsorption via two oxygen atoms localized on the same side of the molecule on two adjacent Si adatoms of the surface.

Such cycloaddition mechanisms are also observed on cubic surfaces such as Si(001),[29] Ge(001),[30] C(001),[31] and SiC(001) (Ref. 32) in the case of small molecules. Our study of the PTCDI/SiC system shows that larger molecules are able to adsorb on hexagonal surfaces. In fact, the adatom-adatom distance on the SiC(0001)-3 × 3 surface, 9.29 Å, may allow direct adsorption of larger molecules via cycloaddition. It is the case of the large H_2Pc molecule which can be anchored on the SiC(0001)-3 × 3 surface via a cycloaddition reaction of two conjugated imide groups with two silicon adatoms in H_2Pc chemisorption.[12] We thus observe the formation of two Si-N bonds in the H_2Pc/SiC(0001)-3 × 3 system and two Si-O bonds in the PTCDI/SiC(0001)-3 × 3 system. With an adsorption energy of -2.36 eV, the PTCDI molecule is more strongly bound to the surface than H_2Pc ($E_{\mathrm{ads}} = -1.36$ eV, calculated using the same six-layer slabs and identical parameters).[12] Indeed, in the STM experiments,[14] the H_2Pc molecule is observed to move from one adsorption site to another on the surface under normal tunnel conditions, while the PTCDI remains fixed on a same adsorption site on the surface, unless external electronic excitation is provided with the STM.[33] Given that the PTCDI molecule does not move on the SiC(0001)-3 × 3 surface it would appear to be a more appropriate candidate for organic functionalization of SiC. On the other hand, the motion of the H_2Pc molecule on the surface can easily be electronically activated via the breaking of only one of the two Si-N bonds, and so would be more suitable in the field of nanomachines.

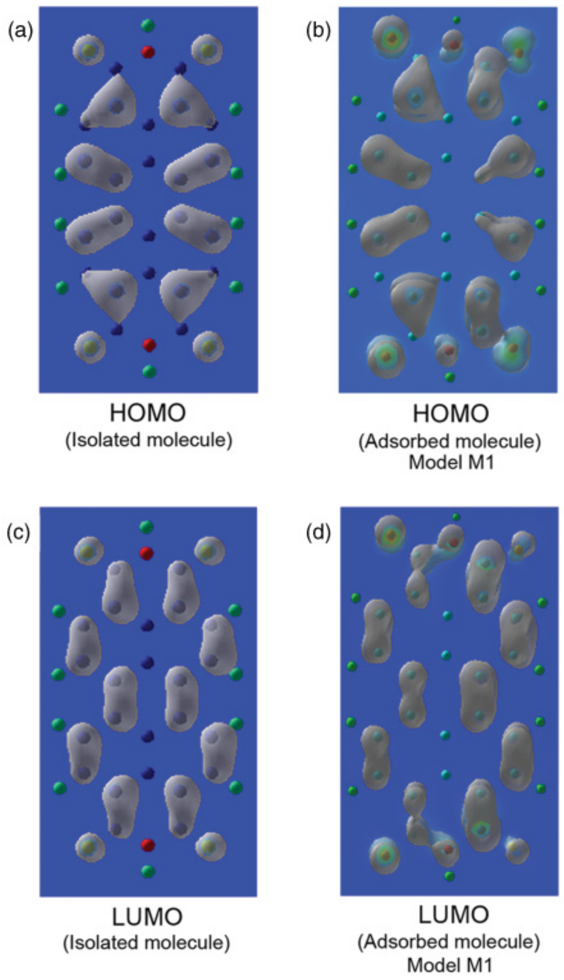

FIG. 8. (Color online) Top view of isodensity maps ($0.02e^-/\text{Å}^3$). (a) HOMO (integrated window between -1.2 and -1.25 eV) and (c) LUMO (integrated window between 0.75 and 0.85 eV) for the isolated molecule; (b) HOMO (integrated window between -1.2 and -1.25 eV) and (d) LUMO (SOMO) (integrated window between -0.25 and -0.35 eV) for the adsorbed molecule.

Finally, the comparison between the H_2Pc and PTCDI molecules emphasizes, in the case of large molecules, a general adsorption mechanism (cycloaddition) that does not depend on the type of involved adsorbed molecule. On the other hand, our study opens up the possibility of functionalizing hexagonal SiC surfaces, which is very important from a technology point of view.

ACKNOWLEDGMENTS

This work was supported by the ANR project MOLSIC (Contract No. ANR-08-NANO-058). It was performed using HPC resources from GENCI-IDRIS (Grant No. 2010-096459).

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