

A new assisted molecular cycloaddition on boron doped silicon surfaces: a predictive DFT-D study

Cite this: *Phys. Chem. Chem. Phys.*, 2014, 16, 12164

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In the framework of the Density Functional Theory (DFT-D), we investigate the phthalocyanine (H_2Pc) molecule adsorption on $SiC(0001)3 \times 3$ and $Si(111)\sqrt{3} \times \sqrt{3}R30^\circ-B$ (SiB) surfaces, and particularly compare the involved molecular adsorptions. In the $H_2Pc-SiC(0001)3 \times 3$ system, the molecular adsorption can be ascribed to a [10+2] cycloaddition. The $H_2Pc-SiB$ system is considered in three cases: defectless SiB surface (denoted SiB-0D) and SiB surfaces presenting one or two boron defects (denoted SiB-1D and SiB-2D respectively). The SiB-0D surface is passivated by a charge transfer from the Si atoms to the boron atoms and therefore no chemical bond between the molecule and the substrate is observed. A similar molecular adsorption as already evidenced in the $H_2Pc-SiC(0001)3 \times 3$ system is involved in the SiB-2D case. In the case of the SiB-1D surface, two Si-N bonds (Si1-N1 and Si2-N2) are observed. One of them, Si1-N1, is nearly similar to that found in the $H_2Pc-SiB-2D$ system, but the Si2-N2 bond is unexpected. The Bader charge analysis suggests that, in the presence of the H_2Pc molecule, the boron atoms behave like an electron reservoir whose availability varies following the involved molecular adsorption process. In the SiB-1D case, charges are transferred from the substrate to the molecule, allowing the Si2-N2 bond formation. Such a kind of molecular adsorption, not yet observed, could be designed by "assisted pseudo cycloaddition".

Received 26th February 2014,
Accepted 28th April 2014

DOI: 10.1039/c4cp00839a

www.rsc.org/pccp

I. Introduction

The development of hybrid organic-inorganic devices at the atomic scale has become an important challenge in the field of nanotechnology.¹⁻³ Among these devices, the combination of semiconductor substrates (such as silicon or silicon carbide surfaces) with a variety of specific functions (chemical, electronic, optical...) that can be realized by functionalizing organic molecules is very promising.⁴⁻¹²

Semiconductor surfaces present a great number of reconstruction possibilities and the presence of dangling bonds (DB's) leads to more or less reactivity in the interaction with the incoming molecules. The resulting conformation and arrangement of the adsorbed molecules on the substrate is thus related to the physical and chemical properties of the final organic-inorganic interface. It depends on a subtle balance between the molecule-molecule and molecule-substrate interactions.⁷

Herein, we investigate the phthalocyanine (H_2Pc) molecule adsorption on $SiC(0001)3 \times 3$ and $Si(111)\sqrt{3} \times \sqrt{3}R30^\circ-B$ (denoted SiB) surfaces, and particularly compare the involved

adsorption mechanisms. Our results allow us to propose a new adsorption mechanism for H_2Pc on the SiB surface. In a previous paper, it was shown that the H_2Pc molecule (Fig. 1) adsorbs on the $SiC(0001)3 \times 3$ surface in a configuration in which only two Si dangling bonds of the surface and two nitrogen atoms of the molecule are involved in the formation of covalent Si-N bonds.¹³ This configuration arises from the

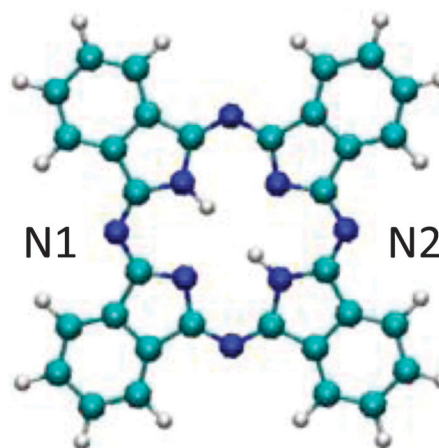


Fig. 1 Ball-and-stick representation of the H_2Pc molecule. Light blue, dark blue and white balls correspond to carbon, nitrogen and hydrogen atoms respectively.

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reaction of two conjugated imide groups in the molecule and the authors proposed to ascribe this molecular adsorption to a [10+2] cycloaddition. They also emphasized that the adsorption of organic molecules on SiC surfaces is possible provided that the molecule contains two reactive and conjugated chemical groups separated by an appropriate distance.^{13,14}

Cycloaddition reactions of small organic molecules (such as ethylene, cyclopentene, butadiene, cyanate...) adsorbed on Si(001), Ge(001) or C(001) surfaces have already been studied.^{15–17} Recently, a [4+2] cycloaddition has also been observed by means of scanning tunneling microscopy (STM) in the early stages of thymine adsorption on the Si(111)7 × 7 surface, and confirmed by DFT calculations.¹⁸ It would therefore be of interest to also investigate the case of larger organic molecules (H₂Pc, perylene-3,4,9,10-tetracarboxylic-3,4,9,10-diimide denoted PTCDI, porphyrin...), and also other semiconducting surfaces such as SiB.^{6–10}

Is a cycloaddition reaction of the H₂Pc molecule with the SiB surface possible? Some arguments play in favor of such a type of molecular adsorption:

(i) The atomic structure of the clean Si(111)√3 × √3R30°-B surface presents some analogies with the SiC(0001)3 × 3 one: in

both surfaces we find silicon adatoms located in the Si top layer and the backbond atoms form a tetrahedral structure (Fig. 2(a) and (b)).

(ii) Upon boron doping underneath the silicon top layer (S5 sites) of the SiB surface, a charge transfer between the Si adatoms and the boron atoms occurs, thus depopulating the Si DB's. The SiB surface is therefore passivated.^{19–22} On the other hand, the presence of boron defects (*i.e.* missing boron atoms) re-establishes the DB's population and one locally find again the atomic structure of the clean Si(111)√3 × √3R30° surface. In this case, the analogies between the atomic structure of the clean SiB and SiC surfaces may thus suggest analogous molecular adsorptions for the H₂Pc molecule on these surfaces.

In the same way as observed in the adsorption of the H₂Pc and PTCDI molecules on SiC(0001)3 × 3 (reactions assigned to pseudo [10+2] and [12+2] cycloadditions respectively^{11–14}), one could expect the formation of two Si–N bonds in the presence of two boron defects separated by an appropriate distance.

The case of the H₂Pc molecule adsorption in the presence of only one isolated boron defect is particularly interesting: such defects mostly occur on the SiB surface, and one can wonder what kind of molecular adsorption is here involved.

In a first step, we extend the previous work¹³ by an electronic structure study of the H₂Pc–SiC(0001)3 × 3 system and further investigate the molecular adsorption. We then consider the H₂Pc–SiB system in three cases: defectless SiB surface (denoted SiB-0D), SiB surfaces presenting two defects (denoted SiB-2D) and finally SiB with one isolated defect (denoted SiB-1D). The energetic and electronic structure studies as well as the involved molecular adsorptions will be investigated and compared to the H₂Pc–SiC(0001)3 × 3 system case.

II. Computational method and models

Calculations are carried out based on density functional theory (DFT) by using the projector augmented wave (PAW) method^{23,24} as implemented in the Vienna Ab initio Simulation Package (VASP).^{25,26} The generalized gradient approximation (GGA) calculations have been performed with Perdew–Burke–Ernzerhof (PBE) exchange–correlation potential.²⁷ Due to the large unit cells used in our calculations (37.16 Å × 37.16 Å × 20 Å and 26.8 Å × 26.8 Å × 30 Å for SiC(0001)3 × 3 and Si(111)√3 × √3R30°-boron reconstructions respectively), the Brillouin zone integration is reduced to the Γ *k*-point. The cut-off energy for plane-wave is equal to 400 eV corresponding to the carbon atom one. Besides, for obtaining the optimized ground state geometries, the conjugate gradient algorithm is used until the residual force is within 0.02 eV Å^{−1}. In order to consider the dispersive interactions missing in our previous paper,¹³ we add the energetic correction term proposed by Grimme in the total energetic calculations (*i.e.* DFT-D approximation).^{28–30}

The Si-rich SiC(0001)3 × 3 reconstruction exhibits dangling bonds located on the top of pyramidal Si structures separated by about 9.3 Å from each other. We adopt the model proposed

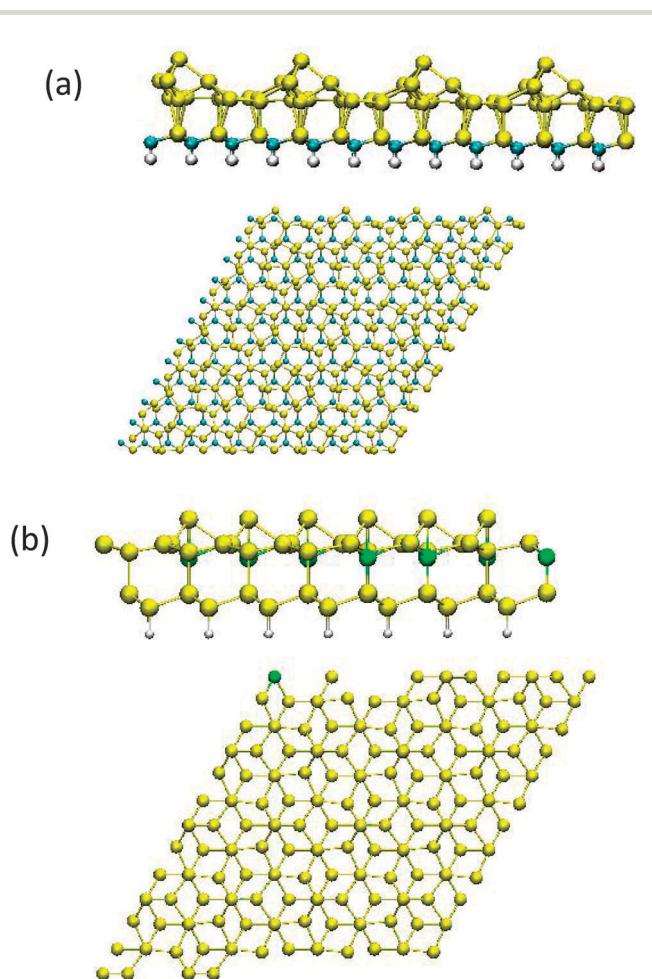


Fig. 2 (a) and (b) Side and top view of the SiC(0001)3 × 3 and SiB unit cell used in the paper respectively. Yellow, green, light blue and white circles correspond to silicon, boron, carbon and hydrogen atoms respectively.

by Schardt *et al.* commonly accepted.³¹ The periodic slab, presented in Fig. 2(a), contains six layers (three layers for the reconstruction, one bilayer of SiC, and one layer of hydrogen atoms). The total number of atoms is 640. The H atoms are added on the back side to saturate the DB's. In the geometry optimization phase, the molecule, the reconstruction layers and the silicon layer of the SiC bilayer are allowed to relax while the carbon and hydrogen layers are kept fixed. In order to estimate the necessity of growing the slab thicker, we have already considered a larger slab involving ten layers (three layers for the reconstruction, three bilayers of SiC and one layer of H atoms) in a previous paper.¹² The same ordering in the adsorption energies was observed and the relative adsorption energy variation was less than 0.1 eV.

The Si(111) $\sqrt{3} \times \sqrt{3}R30^\circ$ -boron, denoted by SiB, is modelled by periodic slabs containing four layers and one silicon adatom layer (Fig. 2(b)). Hydrogen atoms saturate the backside of the slab. The total number of atoms is 256 for the defectless substrate (*i.e.* 16 silicon adatoms, 176 silicon atoms for the 4 layers, 16 boron atoms located in S5 sites of the second layer and 48 H atoms on the bottom of the slab). In the geometry optimization phase, the molecule, the adatoms layer and the three top most layers are allowed to relax while the last silicon and hydrogen layers are kept frozen. The SiB defectless slab has been already successfully used to simulate the adsorption of a nanoporous molecular network on the SiB surface. The simulation of STM images was in good agreement with the experimental STM observations.³²

In the initial states, the molecule in the gas phase (H₂Pc) and the isolated substrates (SiC and SiB surfaces) were geometry-optimized at the same level of theory prior to placing the molecule on the surface. The relaxation of the final states (H₂Pc–SiC(0001) and H₂Pc–SiB systems) is a further geometry optimization step.

The charge transfer occurring between the molecule and the surface was analyzed through a partial charges approach (*i.e.* valence electrons) in the Bader scheme.^{33,34} One indication of the quality of the Bader analysis results is the total number of valence electrons obtained from the integration over all the Bader regions (*i.e.* the conservation of charge). When using the (280 × 280 × 336) grid, the total number of electrons is reproduced with an error less than 10^{−5}. We are able to conclude that the Bader charge is well converged with respect to the used mesh.

In order to highlight the interaction between the H₂Pc molecule and the SiC or SiB surfaces, the electron localization function (*i.e.* ELF) representation has been used.^{35–37} ELF is based on the Hartree–Fock pair probability of parallel spin electrons and can be calculated using density functional theory from the excess kinetic energy density due to Pauli-repulsion.^{38,39} This function produces easily understandable, pictorially informative patterns of chemical bonding and is widely used to describe and visualize chemical bonding in molecules and solids.⁴⁰ The ELF is a measure of the probability of finding an electron near another electron with the same spin related to the Pauli Exclusion Principle.^{41,42}

III. H₂Pc adsorption on the SiC(0001) $\sqrt{3} \times \sqrt{3}$ surface

In our previous paper, the atomic structure and adsorption energy of the H₂Pc–SiC(0001) $\sqrt{3} \times \sqrt{3}$ system were investigated within the periodic DFT using the VASP code in the generalized gradient approximation (GGA) and PAW pseudopotentials. We complete here this study by introducing the dispersive Grimme term.^{28–30}

A view of the relaxed system is shown in Fig. 3(a). We immediately notice that, in the same way as in the GGA approximation case, the H₂Pc molecule is nearly planar and adsorbs on the SiC(0001) $\sqrt{3} \times \sqrt{3}$ surface by forming two Si–N bonds. The calculated adsorption energy and the Si1–Si2, Si1–N1, Si2–N2 and N1–N2 distances are presented in Table 1 and compared to those obtained in the GGA approximation.

The adsorption energy varies from −1.36 eV in the GGA approximation to −3.07 eV in the DFT-D one. Taking the van

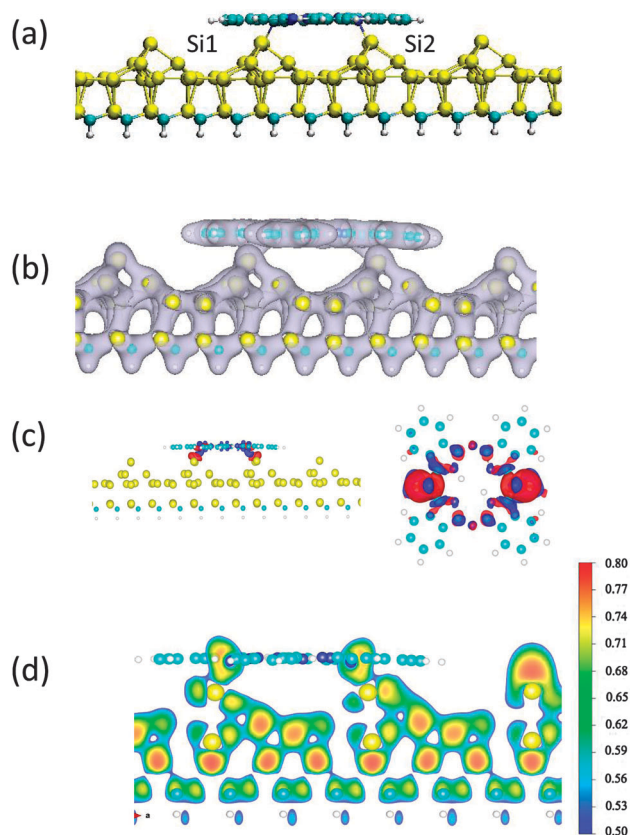


Fig. 3 Side views of the H₂Pc adsorption on SiC(0001) $\sqrt{3} \times \sqrt{3}$: (a) atomic structure of the optimized configuration. The N1 and N2 atoms are located just above the Si1 and Si2 adatoms; (b) charge densities ($\rho = 0.3 \text{ e}^- \text{ \AA}^{-3}$); (c) top view (left) ($\Delta\rho = \pm 0.05 \text{ e}^- \text{ \AA}^{-3}$) and side view (right) ($\Delta\rho = \pm 0.015 \text{ e}^- \text{ \AA}^{-3}$) of the charge density difference. In order to facilitate the interpretation, the atoms of the substrate are removed in the top view. Blue and red plots correspond to positive and negative electronic charge variations respectively; (d) calculated ELF representation. On the right side, the colour code of the ELF is as follows: ELF = 0.8 (in red) indicates an electron localized region, ELF = 0.5 (in blue) corresponds to a delocalized region. The ELF plane cuts through the N1–Si1 and N2–Si2 bonds. Yellow, green, light blue, dark blue and white circles correspond to silicon, boron, carbon, nitrogen and hydrogen atoms respectively.

Table 1 Adsorption energies and Si1–Si2, Si1–N1, Si2–N2 and N1–N2 distances after relaxation calculated by means of DFT and DFT-D methods. In the initial state where the substrate and the molecule are separated, the Si1–Si2 and N1–N2 distances were 9.29 Å and 6.71 Å in the DFT case¹³ and 9.29 Å and 6.78 Å in the DFT-D case

	DFT	DFT-D
Adsorption energy (eV)	−1.36	−3.07
Si1–Si2 (Å)	8.85	8.89
Si1–N1 (Å)	1.88	1.89
Si2–N2 (Å)	1.88	1.88
N1–N2 (Å)	7.16	7.08

der Waals interactions into account thus stabilizes the system to a great extent.

On the other hand, the Si1–Si2, Si1–N1, Si2–N2 and N1–N2 distances only slightly differ in the two approximations and, finally, the van der Waals forces only slightly affect the relaxed atomic structure.

After relaxation, the distances between the two Si adatoms (Si1–Si2) and the two nitrogen atoms (N1–N2) vary from 9.29 to 8.89 Å and 6.78 to 7.07 Å respectively. The Si1–Si2 distance larger than the N1–N2 one before relaxation decreases in the Si–N bond formation, while the N1–N2 distance increases. We also remark that the Si1–N1 (1.89 Å) and Si2–N2 (1.88 Å) distances seem to be reasonable compared to the chemical Si–N bond.

All these results agree with the molecular adsorption described in ref. 13. In that previous paper, the adsorption of individual metal free phthalocyanine molecules on the SiC(0001)3 × 3 surface was studied by means of STM experiments supported by DFT calculations.¹³ In these simulations, a molecular adsorption configuration in which two Si adatom DB's of the SiC surface are involved in the formation of covalent Si–N bonds with two nitrogen atoms of the molecule was determined.

The electronic structure study may give us further information. A first observation concerns the calculated charge densities of the H₂Pc–SiC(0001)3 × 3 system reported in Fig. 3(b): they are clearly located around the Si1–N1 and Si2–N2 bonds. Additional data are given by the charge density difference defined by the difference of the total charge of the relaxed complete system minus the sum of the isolated molecule charge and the isolated substrate charge without further relaxation. The contour plot of the charge density difference induced by the deposition of the H₂Pc molecule on the SiC(0001)3 × 3 surface at their corresponding equilibrium is presented in Fig. 3(c). Blue and red plots correspond to positive and negative electronic charge variation respectively. An electron accumulation in the binding region is observed: the charge variations are essentially located between the N atoms of the molecule and the Si adatoms, corresponding to the Si–N bond formation.

In the presence of the H₂Pc molecule, the Si1 and Si2 adatoms lose charges while the N1 and N2 atoms principally receive any charges. These observations also play in consideration of the above model proposed for the molecular adsorption.

The calculated ELF for the H₂Pc–SiC(0001) system is projected in a perpendicular plane to the SiC surface, crossing the Si1–N1 and Si2–N2 bonds (Fig. 3(d)). The yellow-orange clouds located around

the Si1–N1 and Si2–N2 bonds indicate strong electron localization. These remarks also argue in favour of chemical Si–N bonds.

Finally, comparing, for instance, this molecular adsorption to the [2+2] cycloaddition reaction occurring in one ethylene molecule adsorption on one Si=Si dimer of the Si(001) surface presented in ref. 15, we find no double bond between the Si1 and Si2 adatoms of the SiC(0001)3 × 3 substrate due to the large adatom–adatom distance. We therefore rather deal with a “pseudo [10+2] cycloaddition” in the H₂Pc adsorption on the SiC(0001)3 × 3 surface as reported in ref. 13.

IV. H₂Pc molecule adsorption on the SiB surface

We consider the H₂Pc–SiB system in three cases: defectless SiB surface (SiB-0D), SiB surfaces presenting one (SiB-1D) or two (SiB-2D) defects (*i.e.* missing boron atoms). The corresponding

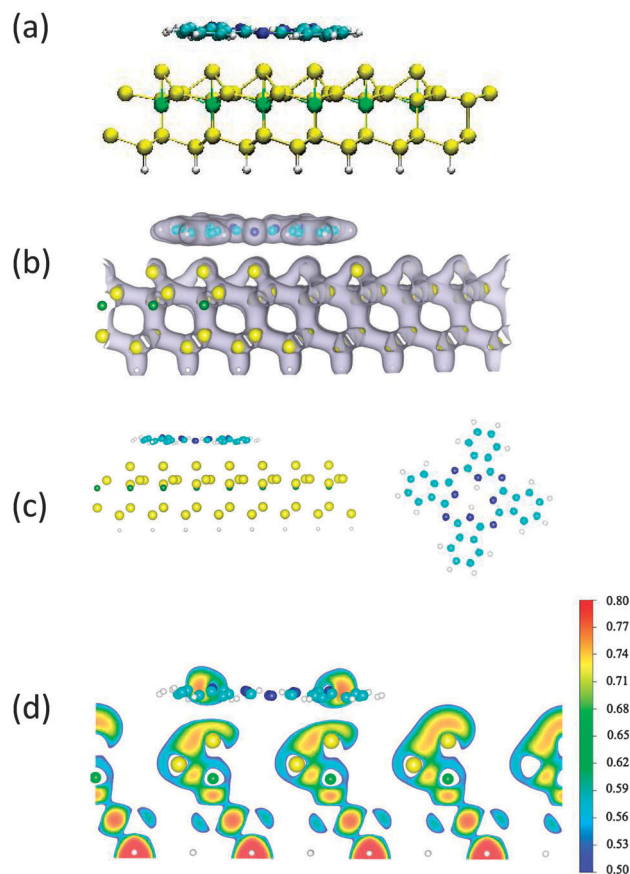


Fig. 4 Side views of the H₂Pc adsorption on the SiB-0D surface: (a) atomic structure of the optimized configuration; (b) charge densities ($\rho = 0.3 \text{ e}^- \text{ \AA}^{-3}$); (c) top view (left) ($\Delta\rho = \pm 0.05 \text{ e}^- \text{ \AA}^{-3}$) and side view (right) ($\Delta\rho = \pm 0.015 \text{ e}^- \text{ \AA}^{-3}$) of the charge density difference. In order to facilitate the interpretation, the atoms of the substrate are removed in the top view. Blue and red plots correspond to positive and negative electronic charge variations respectively; (d) calculated ELF representation. On the right side, the colour code of the ELF is as follows: ELF = 0.8 (in red) indicates an electron localized region, ELF = 0.5 (in blue) corresponds to a delocalized region. The ELF plane cuts through the N1–Si1 and N2–Si2 bonds. Yellow, green, light blue and white circles correspond to silicon, boron, carbon and hydrogen atoms respectively.

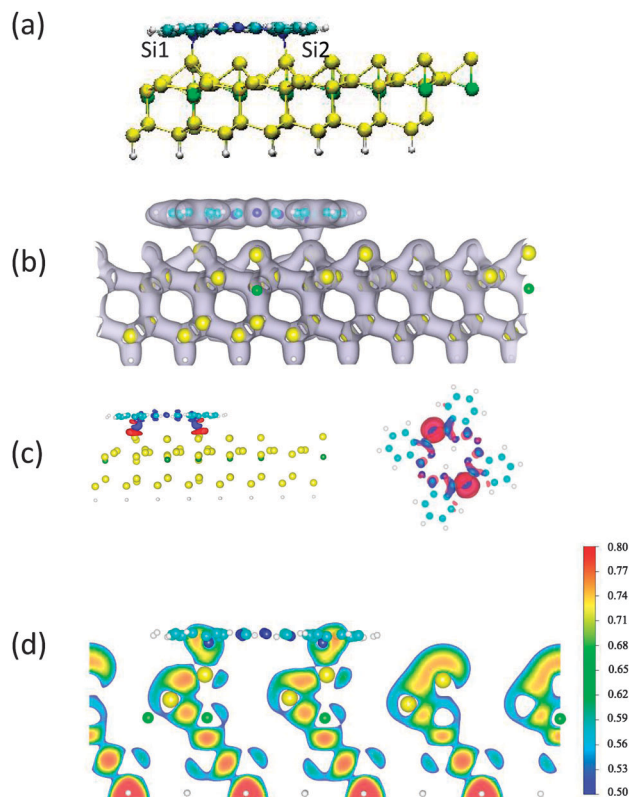


Fig. 5 Side views of the H_2Pc adsorption on the SiB-2D surface: (a) atomic structure of the optimized configuration. The N1 and N2 atoms are located just above the Si1 and Si2 adatoms; (b) charge densities ($\rho = 0.3 \text{ e}^- \text{ \AA}^{-3}$); (c) top view (left) ($\Delta\rho = \pm 0.05 \text{ e}^- \text{ \AA}^{-3}$) and side view (right) ($\Delta\rho = \pm 0.015 \text{ e}^- \text{ \AA}^{-3}$) of the charge density difference. In order to facilitate the interpretation, the atoms of the substrate are removed in the top view. Blue and red plots correspond to positive and negative electronic charge variations respectively; (d) calculated ELF representation. On the right side, the colour code of the ELF is as follows: ELF = 0.8 (in red) indicates an electron localized region, ELF = 0.5 (in blue) corresponds to a delocalized region. The ELF plane cuts through the N1–Si1 and N2–Si2 bonds. Yellow, green, light blue, dark blue and white circles correspond to silicon, boron, carbon, nitrogen and hydrogen atoms respectively.

atomic structures after relaxation are shown in Fig. 4(a), 5(a) and 6(a) respectively, and the adsorption energies calculated in the framework of the DFT-D method as well as the Si1–Si2, Si1–N1, Si2–N2 and N1–N2 distances are reported in Table 2.

IV.(A) H_2Pc molecule adsorption on the defectless SiB surface (SiB-0D)

Let us first investigate the H_2Pc molecule adsorption on the SiB-0D surface. Due to the presence of boron atoms underneath the silicon top layer (S5 sites), a charge transfer from the Si adatoms to the boron atoms occurs. The SiB DB's are then depopulated and the SiB-0D surface is passivated.^{19–22} The adsorption energy is -1.35 eV . The H_2Pc molecule remains planar as shown in Fig. 4(a). It is slightly tilted with respect to the surface: we find a small difference between the Si1–N1 and Si2–N2 distances (2.84 \AA and 2.98 \AA respectively). The Si1–Si2 and N1–N2 distances vary only little compared to the H_2Pc –SiC(0001) 3×3 case.

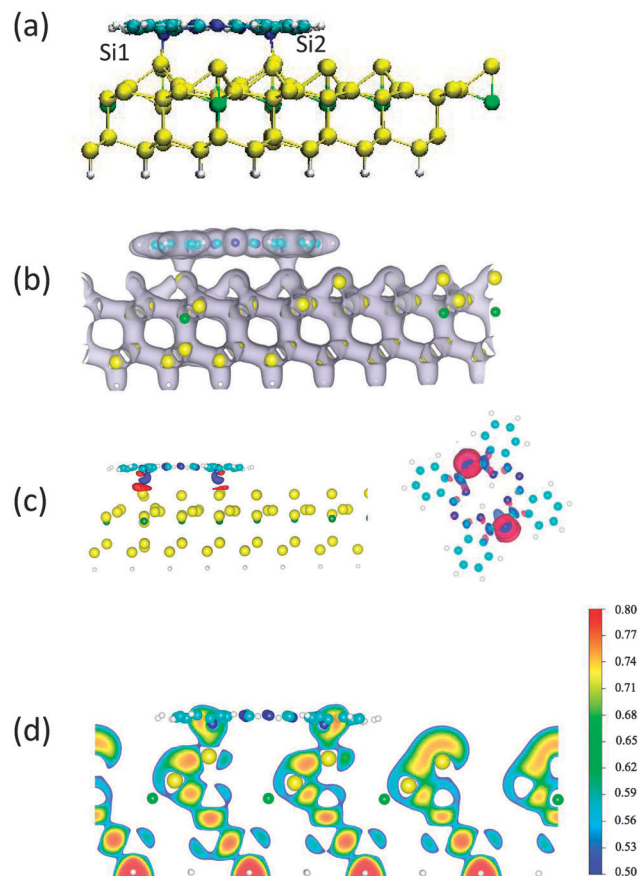


Fig. 6 Side views of the H_2Pc adsorption on the SiB-1D surface: (a) atomic structure of the optimized configuration. The N1 and N2 atoms are located just above the Si1 and Si2 adatoms; (b) charge densities ($\rho = 0.3 \text{ e}^- \text{ \AA}^{-3}$); (c) top view (left) ($\Delta\rho = \pm 0.05 \text{ e}^- \text{ \AA}^{-3}$) and side view (right) ($\Delta\rho = \pm 0.015 \text{ e}^- \text{ \AA}^{-3}$) of the charge density difference. In order to facilitate the interpretation, the atoms of the substrate are removed in the top view. Blue and red plots correspond to positive and negative electronic charge variations respectively; (d) calculated ELF representation. On the right side, the colour code of the ELF is as follows: ELF = 0.8 (in red) indicates an electron localized region, ELF = 0.5 (in blue) corresponds to a delocalized region. The ELF plane cuts through the N1–Si1 and N2–Si2 bonds. Yellow, green, light blue, dark blue and white circles correspond to silicon, boron, carbon, nitrogen and hydrogen atoms respectively.

Table 2 Adsorption energies and Si1–Si2, Si1–N1, Si2–N2 and N1–N2 distances after relaxation calculated by means of the DFT-D method. In the initial state, the Si1–Si2 and N1–N2 distances were 6.70 and 6.78 \AA in the DFT-D case

	H_2Pc –SiB-0D	H_2Pc –SiB-1D	H_2Pc –SiB-2D
E_{ads} (eV)	-1.35	-1.84	-2.73
Si1–Si2 (\AA)	6.75	6.92	6.93
Si1–N1 (\AA)	2.84	1.91	1.84
Si2–N2 (\AA)	2.98	2.01	1.84
N1–N2 (\AA)	6.66	6.48	6.50

The Bader charges, corresponding to the charge difference between the final state (molecule adsorbed on the substrate) and the initial state of the system (isolated substrate and molecule in the gas phase), are reported in Table 3.

Table 3 Calculated Bader charges in the four studied systems in electron (e^-) units

	H ₂ Pc on SiB-0D	H ₂ Pc on SiB-1D	H ₂ Pc on SiB-2D	H ₂ Pc on SiC(0001)3 × 3
Si1 adatom	-0.03	-0.7	-0.82	-0.75
Si2 adatom	-0.02	-0.41	-0.82	-0.76
B1 or Si under Si1	-0.22 (B1)	+0.09 (Si)	+0.09 (Si)	—
B2 or Si under Si2	-0.34 (B2)	-0.31 (B2)	+0.01 (Si)	—
N1	+0.02	+0.23	+0.21	+0.21
N2	+0.01	+0.25	+0.25	+0.22
H ₂ Pc molecule (total charge transfer)	+0.09	+1.58	+2.27	+2.19

The Bader charge analysis indicates only weak charge transfer from the Si1 and Si2 adatoms to the H₂Pc molecule. The H₂Pc molecule total charge transfer is very small (+0.09 e^-) as expected, the SiB-0D surface being passivated. The charge variations of the B1 and B2 atoms located underneath the Si1 and Si2 adatoms are $-0.22 e^-$ and $-0.34 e^-$ respectively. The total charge variation for the H₂Pc molecule being only +0.09 e^- , we deduce that the involved charges remain in the substrate.

Further information is given by the electronic study. The calculated charge densities (Fig. 4(b)) and charge density difference (Fig. 4(c)) as well as the ELF do not show any charge between the molecule and the substrate: there is no chemical bond. Effectively, the SiB-0D surface is passivated.

IV.(B) H₂Pc molecule adsorption on the SiB-2D surface

Let us now turn to the case where the H₂Pc molecule is adsorbed on the SiB-2D surface. The atomic structure of the H₂Pc-SiB-2D system after relaxation is shown in Fig. 5(a). Two boron atoms, missing in the SiB surface, are here substituted by Si atoms. The two Si adatom dangling bonds located above these defects are now again populated, favouring the formation of two Si-N bonds. The adsorption energy is now $-2.73 eV$. The Si1-Si2 and N1-N2 distances (6.93 Å and 6.50 Å respectively) are closer than in the H₂Pc-SiC(0001)3 × 3 system, and the Si-N bonds (1.84 Å) are shorter. By comparing this behavior to that of the H₂Pc-SiC(0001)3 × 3 system, analogous molecular adsorption might be considered. The electronic study and Bader charge analysis will help us in this investigation.

In Fig. 5(b), we now observe the presence of charge densities between two N atoms of the H₂Pc molecule and two Si adatoms (located above two boron-defects) indicating two Si-N bond formation. The charge density differences shown in Fig. 5(c) emphasize a loss of charge (red clouds) on the two Si adatoms, whereas the Si-N bond receives the most important part of them, the remaining charges being transferred on the molecule (blue clouds). In the same way as already observed in the H₂Pc-SiC(0001)3 × 3 case, the ELF shows yellow-orange clouds located between the Si1 and N1 atoms, Si2 and N2 atoms respectively.

The Bader charge calculations (Table 3) indicate similar charge transfers in the H₂Pc-SiB-2D and H₂Pc-SiC(0001)3 × 3 systems, confirming analogous molecular adsorption in the two cases. The electrons move from the populated Si adatom DB's ($-0.82 e^-$ and $-0.76 e^-$ in the SiB-2D and SiC(0001)3 × 3 cases respectively) to the H₂Pc molecule (+2.27 e^- and +2.19 e^-

respectively). In the same way, the N1 and N2 atoms receive very close charges.

IV.(C) H₂Pc molecule adsorption on the SiB-1D surface

In the H₂Pc-SiB-1D system, one boron atom is substituted by one Si atom on the SiB surface. Only one Si adatom dangling bond, located above this defect, is therefore expected to be populated and become reactive, leading to one Si-N bond formation. The atomic structure of the H₂Pc-SiB-1D system after relaxation is shown in Fig. 6(a). Surprisingly, two Si-N bonds seem to be formed. The adsorption energy is $-1.84 eV$, intermediate between the SiB-0D and SiB-2D cases, but closer to the SiB-0D one. The presence of a boron defect thus stabilizes the system with respect to the H₂Pc-SiB-0D one. The Si1-Si2 and N1-N2 distances (6.92 and 6.48 Å respectively), closer than in the H₂Pc-SiC system, are nearly the same as those found in the H₂Pc-SiB-2D one. The Si-N distances, larger than in the H₂Pc-SiB-2D system, are here asymmetric (Si1-N1 = 1.91 Å; Si2-N2 = 2.01 Å). The smallest, Si1-N1, involves the Si1 adatom located just above the boron defect and might correspond to a chemical Si1-N1 bond. But what about the Si2-N2 bond? Finally, the atomic structure of the H₂Pc-SiB-1D and H₂Pc-SiB-2D present some analogous characteristics: two Si-N bonds are observed but the nature of these two bonds needs here to be deeply investigated.

The charge densities of the H₂Pc-SiB-1D system are reported in Fig. 6(b). We find that the charge densities between the molecule and the substrate lead to two Si-N bonds as already observed in the SiB-2D case. The differences between the two Si-N bonds are more marked in the charge density difference shown in Fig. 6(c). One of the Si-N bonds, Si1-N1, just above the boron defect, is nearly similar to that found in the H₂Pc-SiB-2D system and might correspond to an analogous molecular adsorption as proposed in Section IV.(B). In the second Si-N bond, Si2-N2, the distance between the Si adatom and the N atom (2.01 Å) is larger than in the Si1-N1 bond (1.91 Å), indicating a weaker bond. We moreover observe a smaller red cloud located in the Si2 adatom DB. In the ELF study shown in Fig. 6(d) and 5(d), the H₂Pc-SiB-1D and H₂Pc-SiB-2D systems present similar behaviors: the electrons located between the Si and N atoms suggest a chemical bond formation. In the SiB-1D case, a small asymmetry between the Si1-N1 and Si2-N2 bonds can be observed, particularly in the yellow/orange region between the Si2 and N2 atoms.

In the H₂Pc-SiB-1D system, only one charge originating from the Si1 DB seems to be involved. We observe two Si-N

bonds, although that one of the two electronic charges that should be involved in the formation of these two bonds is missing. One can wonder if the missing charge originates from the substrate or from the molecule.

Studying the Bader charges provides a deeper understanding of the chemical bonds formation and particularly the Si2–N2 one. Concerning the Si1–N1 bond, the Bader charge transfers ($-0.7 e^-$ for Si1, $+0.23 e^-$ for N1), reported in Table 3, are similar to those observed in the H₂Pc–SiB-2D and H₂Pc–SiC(0001)3 × 3 systems. In the Si2–N2 bond, the Si2 adatom gives a significative charge ($-0.41 e^-$) despite the presence of the boron atom underneath Si2, and the N2 atom charge is nearly the same as in the SiB-2D and SiC surface. The H₂Pc molecule receives $+1.58 e^-$, more than half of the charge received in the H₂Pc–SiB-2D case.

Let us finally consider the boron atom charges. In the case of the SiB-1D surface, the charge difference of the Si atom (located in the S5 site underneath the Si1 adatom) remains nearly the same ($+0.09 e^-$) while the B2 atom gives $+0.31 e^-$. A part of this B2 atom charge in the Bader scheme is transferred to the H₂Pc molecule whose charge gain is $1.58 e^-$, more than half of the charge variation in the SiB-2D surface case ($+2.27 e^-$).

The boron electrons are easily perturbed by the presence of the H₂Pc molecule. They behave like an electron reservoir whose availability varies following the involved molecular adsorption: the charges remain in the substrate in the SiB-0D surface case, and could be transferred to the molecule in the SiB-1D surface case, allowing the formation of the unexpected Si2–N2 bond.

Such a molecular adsorption has, to our knowledge, not yet been observed and could be designed by “assisted pseudo-cycloaddition”.

V. Conclusion

In this paper, we investigated the H₂Pc molecule adsorption on the SiC(0001)3 × 3, SiB-0D, SiB-1D and SiB-2D surfaces. We particularly focused on the involved molecular adsorption. In our study on the H₂Pc–SiC(0001)3 × 3 system, we first completed our previous DFT calculations by introducing the dispersive Grimme term (DFT-D approximation). The van der Waals interactions stabilize the system to a great extent, but only slightly affect the relaxed atomic structure found in ref. 13. The electronic structure study (charge densities, charge density differences, ELF) and Bader charges analysis confirm the molecular adsorption presented in ref. 13.

Comparing the molecular adsorption involved in the H₂Pc–SiC(0001)3 × 3 system to the [2+2] cycloaddition reaction occurring in the ethylene adsorption on Si=Si dimers of the Si(001) surface,¹⁵ we find no double bond between the Si1 and Si2 adatoms of the SiC(0001)3 × 3 substrate due to the great distance between the adatoms. We therefore rather deal with a “pseudo [10+2] cycloaddition”.

Turning to the H₂Pc–SiB system we distinguished three cases: defectless SiB surface (SiB-0D), SiB surfaces presenting one (SiB-1D) or two (SiB-2D) defects (missing boron atoms).

In the H₂Pc–SiB-0D system, the SiB-0D surface is passivated by a charge transfer from the Si adatoms to the boron atoms. The H₂Pc molecule remains planar and no chemical bond between the molecule and the substrate is observed.

In the SiB-2D surface, the two Si adatom DB's located above the two boron defects are populated favouring two Si–N bond formation. A similar adsorption to the one observed in the H₂Pc–SiC(0001)3 × 3 system is suggested for the H₂PC molecule adsorption on the SiB-2D surface.

In the SiB-1D surface, one boron atom is substituted by a Si atom. This boron defect stabilizes the H₂Pc–SiB-1D system with respect to the H₂Pc–SiB-0D one. Two Si–N bonds (Si1–N1 and Si2–N2) are observed although that one of the two electrons that should be involved in the two bonds is missing. The electronic structure investigations, and particularly the charge density difference calculations show differences between the two Si–N bonds. The Si1–N1 bond, nearly similar to that found in the H₂Pc–SiB-2D system, might correspond to an analogous adsorption as that proposed in the SiB-2D case. The Si2–N2 bond seems to be weaker and a small lack of charge is observed in this bond. The Bader charge analysis suggests that, in the presence of the H₂Pc molecule, the boron atoms behave like an electron reservoir whose availability varies following the involved process. In the SiB-1D case, the charges are transferred from the substrate to the molecule, allowing the unexpected Si2–N2 bond formation. Such a molecular adsorption could be designed by “assisted pseudo-cycloaddition”.

No experimental study on the H₂Pc molecule adsorption on the SiB surface has yet been realized. Our present study is therefore predictive and should stimulate further experimental work in this field.

Acknowledgements

This work was performed using HPC resources from GENCI-IDRIS (grant 2012-092042) and the supercomputer facilities of the Mésocentre de calcul de Franche-Comté. The French Agency ANR (ANR-09-NANO-038) has supported this work.

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