Formation of \(\pi\)-coupled organic wire on the Si(001)[2 \times 1] surface

Alain Rochefort *, Alexandre Beausoleil

Département de génie Physique and Regroupement québécois sur les matériaux de pointe (RQMP), École Polytechnique de Montréal, C.P. 6079, Succ., Centre-ville, Montréal, Qué., Canada H3C 3A7

Received 30 July 2004; in final form 29 October 2004

Abstract

The stability and electronic properties of highly packed 1-hexyl-naphthalene (HNap) molecular wire on Si(001) have been studied with first principles DFT method. HNap assembles into a 1D arrangement on the Si(001)[2 \times 1] surface on which molecules adopt a commensurate structure along a dimer row with an intermolecular distance of 3.8 Å. HNap is attached to the surface through the hexyl chain, and stands normal to the surface. This highly packed structure leads to the formation of delocalized \(\pi\)-orbitals over the entire wire but essentially localized on the naphthalene counterpart, and well separated from the Si surface states. Cohesion energy within the wire arises from a significant attraction between hexyl chains, and to a weaker stabilizing \(\pi-\pi\) interaction between naphthalenes.

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1. Introduction

Future development of high performance organic electronic component such as transistor is strongly dependant on our understanding and control of \(\pi\)-electron overlap in conjugated molecules or polymers that is responsible for electrical conduction. Typical organic electronic materials are usually characterized by weak \(\pi\)-overlap, and hence lead to a rather low carrier mobility (<1 cm²/Vs) material. After improving intermolecular \(\pi\)-overlap by exploiting different molecular configurations [1,2] and self-assembling characteristics through a judicius choice of functionnal groups [3,4], one can expect a radical change in transport regime from slow polaronic to fast band-transport [1,2,5].

The more direct route to improve \(\pi\)-overlap in organic crystals such as oligophenylene compounds [6,7] or other type of conjugated polymers [8] consists in applying high pressure conditions (≈ 5 GPa) on the materials. Another possibility is by choosing appropriate substituents on the molecules to help molecular units to closely stack through intermolecular bonds such as hydrogen bonding [3,4]. On the other hand, there is few experimental examples of self-assembled monolayer (SAM) on surfaces where significant \(\pi-\pi\) interaction has been directly demonstrated, [9] but there are several others in which its presence was mentionned or proposed [10,11]. Most of recent experiments on SAMs were focusing on the thiols/Au system for which one has to compromise between the strength of the molecular adhesion on the surface via the –SH anchoring group, and the ability of an ensemble of molecules to form a large and well-ordered domain [12–14].

Other specific efforts on the growth of SAMs on semiconducting single-crystal [10,15–20] were attempting to form strong covalent bonding between an organic molecule and the surface. Straight lines of grafted styrene molecule were successfully prepared along the dimer row direction of the Si(001)[2 \times 1] surface [10]. These molecular lines were made of more than 30 styrene molecules well-separated by 3.8 Å, which corresponds to the distance between Si dimer on the hydrogen-terminated
Si(001)[2 × 1] surface. This self-directed growth approach produces a closely packed and well-defined molecular assembly that should favor a significant π-overlap between conjugated molecules.

In this study, we present the results of first principles DFT-LSD calculations on the structural and electronic properties of 1-hexyl naphthalene (HNap) assembled on the Si(001)[2 × 1] surface. The main interest in HNap molecule for potential electrical transport applications is the presence of the C₆ alkyl chain that should allow to electronically isolate the π-rich naphthalene (Nap) fragment from low binding energy states of the Si cluster. For the case of stacked HNap molecule in an ordered 1D structure, we are anticipating to create a π-resonant intermolecular channel near Fermi energy which is essentially localized in the Nap region, and where band conduction or resonant tunneling can efficiently take place.

2. Computational details

The electronic structure calculations were performed with the density functional theory (DFT) NwChem [21,22] software package within Local Spin Density (LSD) approximation. The Vosk–Wilk–Nusair (VWN) potential [23], which is thought to represent the LSD limit, has been used. This VWN potential within DFT formalism was shown to provide an accurate description of physical properties of complexes containing a mixture of organic and metallic species [24]. We used standard all-electron double-ζ basis sets for carbon, silicon and hydrogen atoms. During the geometry optimization, the adsorbed organic fragments were fully optimized while the structure of the remaining silicon cluster which modeled the H-terminated Si(001)[2 × 1] surface was fixed. Density of states (DOS) plots were generated by convoluting the computed electronic structure with a 50:50 combination of Gaussian and Lorentzian functions. In order to analyze the nature of the energy bands, we performed projection on the density of states where each molecular orbital was weighted by the contribution obtained from a Mulliken analysis for a specific fragment of the complex.

3. Results and discussion

3.1. Structural properties

Typical optimized cluster models obtained from the study of molecular wire formation are shown in Fig. 1, where two 1-hexyl-naphthalene (HNap) molecules form C–Si covalent bonds along the dimer row direction of the reconstructed Si(001)[2 × 1] surface. In this study, we considered molecular assemblies made of one, two and four HNap molecular units. As shown in Fig. 1, HNap molecules adopt an upright conformation where the tilt angle of alkyl chains from the surface normal strongly depends on the orientation of surface dangling bonds or terminal hydrogen atoms [10,15,16]. In general, the geometry of the alkyl chain tends to respect the sp³ coordination of surface Si atoms to form a Si–C covalent bond in a similar orientation than the Si–H bond.

![Fig. 1. Typical molecular models of optimized complexes in which two 1-hexyl naphthalene molecules are adsorbed on a Si(001)[2 × 1] surface. Model 2 represents a perfectly aligned arrangement while in model 2', one of the molecule is rotated by 180°.](image)
In addition, the interplanar distance between face-to-face aromatic rings is similar to the separation between two dimer rows, i.e., 3.8 Å. This result is in good agreement with previous work on the self-directed growth of styrene on Si(100) surface [10]. An important consequence of such a molecular alignment of the aromatic rings is the resulting short distance between hexyl chains where the shortest C–C distance is 3.8 Å. This intermolecular distance is similar to the interchain distances reported for solid state hexane and other alkanes [25]. Furthermore, the close proximity of HNap units we found on Si surface also suggests that an additional energy could contribute to the attractive energy that is related to the existence of π–π interaction between aromatic naphthalene fragments.

Fig. 2 shows different dissociation energies \( D_e \) for the first and second R–Si bond where R is HNap or H for complexes containing one (1) or two (2, 2’) molecular units. The dissociation paths A and C give energies for homolytic bond breaking where the final products are doublet states, while the path B considers the dissociation into an alkene and the H-saturated Si cluster. In complex 1, a single HNap molecule is bonded to the surface, and the dissociation energy for homolytic Si–C bond breaking is relatively high, i.e., 3.61 eV (83 kcal/mol). Surprisingly, this value is in the same range as the energy needed to remove a hydrogen atom from a similar site on the surface, i.e., 3.64 eV (84 kcal/mol). Considering the usual overestimation of \( D_e \) within DFT-LDA limits, this last value agrees well with reported Si–H bond dissociation enthalpies of Si-based compound [26]. The fact that dissociation energy for Si–HNap and Si–H is quite similar suggests that the two dissociation processes should compete. On the other hand, the calculated energy difference between path B and A is around 1.8 eV, and clearly indicates that the dissociation of the Si–H bond would constitute the more energetically demanding process and possibly the limiting step in the reaction.

The more interesting results occur with molecular wires made of at least two HNap units. Following path A for complex 2, the dissociation energy for the first HNap unit is 3.88 eV (90 kcal/mol), and the value of \( D_e \) slightly decreases to 3.75 (86 kcal/mol) for the remaining HNap molecule neighboring a Si dangling bond. A similar trend is observed for the dissociation path B. Hence, the presence of a second HNap molecule improves the stability of the first HNap by 0.27 eV (6 kcal/mol). This improved stability or cohesion energy is related to an attractive intermolecular interaction. In order to quantify the different energy involved, we have calculated the energy associated to two isolated hexane molecules in a configuration similar to the complex of Fig. 1. We found an attractive energy of 0.19 eV (5 kcal/mol) between two parallel C–C hexane chains. Hence, this gives a remaining attractive π–π interaction of approximately \( 0.27–0.19 \) eV = 0.08 eV (2 kcal/mol). This additional cohesion energy [27] induced by π–π interaction agrees well with the MP2 calculated binding energies of naphthalene or benzene dimers [28].

This improved stability through π–π stacking is nicely supported by the results obtained for complex 2’ where one of the HNap units was rotated by 180° around the normal axis (see Fig. 1). Even if the complex is significantly stable in this specific geometry, the π–π overlap is clearly smaller than when HNap units are perfectly stacked as in complex 2. Consequently, the energy needed to remove the first HNap molecule, 3.78 eV, is smaller than when π–π overlap is maximized such as in complex 2, i.e., 3.88 eV. It is also interesting to note that the Si dangling bond tends to stabilize HNap on the surface. For example, \( D_e \) of the second HNap unit in complex 2, 3.75 eV (86 kcal/mol), is slightly higher than when the Si dangling bond is saturated with hydrogen, 3.61 eV (83 kcal/mol), such as in complex 1. This last observation with dangling bond is also valid for Si–H bond dissociation, where \( D_e \) for the second hydrogen (3.79 eV) is slightly higher than for the first hydrogen atom (3.64 eV).

Finally, the results obtained on a four (4) HNap units wire show similar structural properties such as a com-
mensurate structure of HNap molecules along the dimer row direction on the Si(001) surface, and is characterized by a relatively short interplanar distance of 3.8 Å. Since we have limited our study to final products, the energetics of the entire surface reaction path involving a chain reaction from the adsorption of the insaturated molecule, followed by hydrogen abstraction to complete the coordination of the adsorbate and to create the next Si dangling bond need to be elucidated. Nevertheless, once HNap is assembled on the Si(001) surface, it forms a quite stable low dimensional structure in which the molecular units are closely packed and where we observe a significant delocalization of frontier $\pi-\pi^*$ orbitals through $\pi$-coupling.

3.2. Electronic properties

We have previously shown that a substantial dispersion of valence ($\pi$) and conduction ($\pi^*$) bands occurs for arenes-assembled wires in which the interplanar distance is in the range of 3.3–4.0 Å [5]. For short interplanar distances, the transport property between units of the molecular assembly (lateral transport) was theoretically predicted to show a drastic transition from a low mobility polaronic transport to an efficient band transport regime. The formation of well delocalized wavefunction in the vicinity of the band gap is clearly responsible of this regime transition. In the following section, we emphasize the variation of electronic properties of the molecular wire as a function of the number of HNap units in the assembly.

Fig. 3 shows the density of states (DOS) of complex 2 on which we also have projected the contribution of 1-hexyl naphthalene units, and Fig. 4 gives a representation of individual wavefunction of states in the vicinity of the HOMO–LUMO gap (HLG). This last figure confirms that the electronic interaction of HNap with the Si cluster is limited to the region where bonds occur, i.e., near the terminal atoms of the alkyl chain. Isolated HNap molecule has a large HLG of 3.4 eV, where the HOMO and LUMO are $\pi$ and $\pi^*$ orbitals respectively, both essentially localized on the naphthalene fragment. On the other hand, the band gap found for the Si(001) model (Si$_{29}$H$_{30}$) cluster (2.8 eV) is much larger than bulk value (1.2 eV), but is consistent with band gaps found for confined Si clusters and quantum dots with similar size [29]. The HLG for HNap–Si complexes is approximately 2.3 eV, the HOMO is centered on the naphthalene region of HNap while the LUMO is localized on the Si cluster. This indicates that the HOMO of the HNap assembly lies in the gap of the Si cluster as identified by the down arrow in Fig. 3.

The HOMO–LUMO separation of HNap is not significantly influenced by the Si cluster to a point where the $\pi-\pi^*$ gap (3.4 eV) of HNap in complex 1 is similar to the isolated HNap case (3.4 eV). Then, we can assume that a change in HLG in the molecular assembly would essentially be related to intermolecular interaction between HNap units. Hence, once the HNap units are closely stacked and separated by 3.8 Å on the Si(001) surface, the $\pi-\pi^*$ separation (indicated by arrows in Fig. 4) decreases sharply from 3.4 to 2.9 eV (3.1 eV for complex 2), to 2.7 eV for respectively, one, two, and four molecular unit wires (see also Fig. 3). The decreasing $\pi-\pi^*$ separation with the number of molecular units in the wire is related to the existence of substantial $\pi$-interaction between assembled molecules that tends to delocalize and disperse the valence and conduction bands, and gradually close the gap [5]. In addition, based on extended Hückel theory calculations on oligoacenes such as benzene, naphthalene and anthracene-based molecular wires in a similar packed configuration [30], we are expecting that this decreasing $\pi-\pi^*$ separation should converge rapidly to a stable value once the assembly contains more than 10 molecular units.

Similarly to the case of 4,4’-biphenylidithiol [5], the packing of individual valence band $\pi$-orbital into a 1D structure leads to the formation of an anti-bonding $\pi^*$-stacked band, and reversely, the packing of conduction band $\pi^*$-orbitals gives an overall bonding $\pi$-stacked band (see Fig. 4). These delocalized $\pi$-stacked bands create new electron/hole transport channel, in which a resonant tunneling can efficiently take place. The creation of well delocalized wavefunction along the molecular assembly appears the more interesting property for molecular electronic applications. This type of organic assembly promises to show strong modulations of the current and a significantly high mobility [1,2,5].
4. Conclusions

The results of our DFT-based calculations predict that 1-hexyl naphthalene can form a stable and tightly bound 1D-dimensional nanostructure on the Si(001) surface. The cohesion and stability of the molecular wire is due to two attractive interactions: (1) between anchored alkyl chains, and (2) to a lesser extent by π–π overlap between aromatic fragments. The formation of a 1D stacked structure with a short intermolecular distance of 3.8 Å has an important influence on the resulting electronic properties. Firstly, the HOMO–LUMO separation of the active HNap packing decreases with the number of molecules in the wire, and should converge to a stable value for longer wire. Secondly, the closed packing of HNap molecules induces the formation of well-delocalized wavefunctions along the 1D direction, that are reminiscent of π–π interaction of frontier orbitals. Finally, this study shows that silicon substrate constitutes an appealing materials for the creation of well-organized and stable nanostructures for future molecular electronic applications.

Acknowledgements

This work was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC). A.B. acknowledges NSERC and the Groupe de recherche en physique et technologie des couches minces (GCM) for summer scholarships. We also thank the Réseau québécois de calcul haute performance (RQCHP) for providing computational facilities.

References

[27] The given cohesion energy was not corrected from basis set superposition error (BSSE).