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How to Fabricate a Surface-Grafted Polythiophene on H-Si(100)2×1 Surface via Self-Assembling and in Situ Surface Polymerization: A Theoretical Guide

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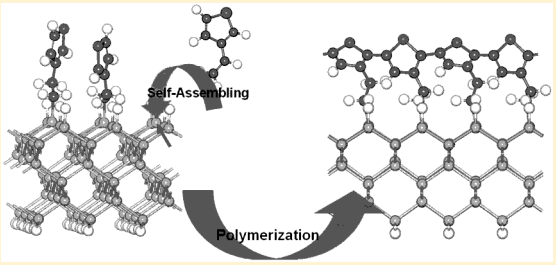
Supporting Information

ABSTRACT: Based on density functional theory calculations, we have studied the self-assembled growth of thiophene substituted alkenes, [H_2C═CH-(CH_2)$_n$-thiophene] on hydrogen-terminated H-Si(100)2×1 and H-Ge(100)2×1 surfaces into aligned one-dimensional (1D) molecular arrays which are chemically bonded to the surfaces via the alkane chain. The thiophene rings at the top end of the molecular arrays are situated side by side and can undergo an in situ polymerization reaction into polythiophene once radicals are introduced to the thiophene rings, thereby forming polyalkylthiophene-Si/Ge(100)2×1 surface-grafted polymers. Like most of conductive polymers, these surface single polymer chains exhibit semiconducting character and can be made conductive either by p-doping or by applying an external electric field. More importantly, both surface-grafted polymers and substrates retain their electrical properties, and the polythiophene chains are the sole conductive channels in the structures. Our findings put forth a new way to fabricate conductive polymeric molecular wires on traditional semiconducting substrates, and could find potential application in nanoelectronic devices.



1. INTRODUCTION

In the past decades, scientists and engineers have been struggling to fabricate single conductive molecular wires or conductive polymer chains on traditional semiconductor substrates in order to satisfy the ongoing miniaturization of electronic devices. Recently, using ultrahigh vacuum (UHV) scanning tunneling microscopy (STM),[1,2] experiments have demonstrated that many olefins are able to self-assemble on a hydrogen-passivated H-Si(100)2×1 surface to form one-dimensional (1D) aligned molecular arrays. For example, Lopinski et al. have proven in their experiments that styrene can grow into 1D molecular array on a H-Si(100)2×1 surface.[3] Via ethenyl group, a styrene molecule bonds easily with a H-empty silicon site, created by atomic force microscopy (AFM) or scanning tunneling microscopy (STM) nanopatterning technologies. The adsorption breaks the ethylene C−C π-bond and generates a C-centered radical that can extract a H atom on the adjacent surface Si atom to form ethane, resulting in a new H-empty silicon site for subsequent styrene adsorption. As such radical chain reaction process,[3−7] a 1D surface absorbed phenyl ethane molecular array is formed eventually. Other examples like allyl mercaptan,[8] long chain alkene (C_8−C_{14}),[9] benzaldehyde,[10] and phenylacetylene (PA)[11] have been demonstrated to self-assemble and form 1D molecular arrays on H-Si(100)2×1 surfaces.

Following the same mechanism, a thiophene-substituted alkene, H_2C═CH-(CH_2)$_n$-thiophene [Figure 1a], should be able to adsorb to a H-empty silicon site on either H-Si(100)2×1 or H-Ge(100)2×1 surfaces and further grow into a 1D thiophene-substituted alkane molecular array along the dimer row [011] direction (Figure 1). Based on density function theory (DFT) calculations, in this study we investigated the adsorption reaction paths for H_2C═CH-(CH_2)$_n$-thiophene, including ethylene (n = 0), propylene (n = 1), butylene (n = 2), and amylene (n = 3) on H-Si/(100)2×1 and H-Ge/(100)2×1 surfaces. We demonstrate that it is very feasible for these H_2C═CH-(CH_2)$_n$-thiophene molecules to adsorb and grow into 1D aligned molecular arrays along [011] direction because the molecular adsorption energies are much higher than activation energies for molecular array growth.

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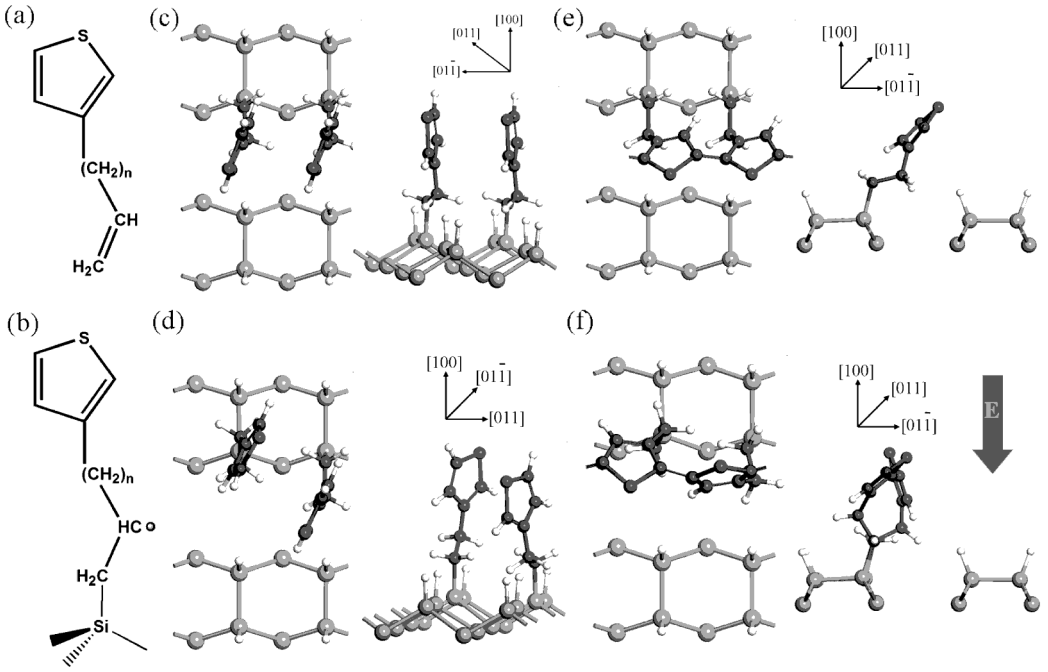

Figure 1. (a) Thiophene-substituted alkenes, H_2C═CH-$(CH_2)_n$-thiophene; (b) H_2C═CH-$(CH_2)_n$-thiophene absorbed on a H−Si(001)2×1 surface with a C-centered radical; top and side views of (c) homolateral and (d) heterolateral configurations of a thiophene substituted ethane molecular array on the silicon surface; top and side views of (e) homolateral and (f) heterolateral configurations of surface polyethylthiophene, respectively. White, gray, red, and yellow spheres represent hydrogen, carbon, sulfur, and silicon atoms, respectively, and the same notations are used in the following figures.

These molecular arrays are chemically bonded to the surfaces via the alkane chains; meanwhile, the thiophene rings are located side by side at the top end of the molecular array and can then polymerize into polythiophenes if radicals are introduced by AFM or STM tips, eventually forming polyalkylthiophene-Si/Ge(100)2×1 surface-grafted single-line polymers. The newly formed surface-grafted polythiophene chains are partially conjugated and exhibit intrinsic semiconducting characters as with most conductive polymers. They can be made to be conductive either by p-doping or by applying an external electric field (EEF). The band gaps and the electrical conductivities will depend on the dihedral angles of adjacent thiophene rings among polyalkylthiophene-Si/Ge(100)2×1, which are subjected to the length of alkanes linked to the surfaces. It is also found that partially conjugated polythiophene chains are the sole conductive channels in the polymer/surface structures.

Single conjugated polymers, especially polythiophene and its derivatives, such as poly(3-alkylthiophene)s, have been considered as promising molecular wires for next generation nanoelectronics, solar cells, light emitting diodes, and sensors due to their excellent conductivity, chemical stability, and relative ease in synthesis.[12−22] Great efforts have been invested in single polythiophene chain fabrications on surface substrates. For example, Sakaguchi et al. have shown experimentally that two different kinds of thiophene monomers on an iodine-covered gold surface can create highly ordered conjugated copolymer chains with different electronic structures by electrochemical polymerization.[23,24] While, the synthesized polymer chains adhere to the Au surfaces with van der Waals interactions only and thus can be peeled off when the temperature is increased. Therefore, it is not meaningful for real application. As Lipton-Duffin et al. indicated that one of the greatest challenges in surface chemistry is to assemble aromatic building blocks into ordered structures that are mechanically robust and electronically interlinked, i.e., held together by covalent bonds.[25] They have demonstrated the synthesis of polyphenylene molecular wires by surface-confined polymerization on crystal Cu surfaces.[26] However, fabrication of a conductive polymer chain on a metallic surface is not very useful for electronic applications.

In comparison, surface-grafted single-line polyalkylthiophene-Si/Ge(100)2×1 are chemically bonded to the Si or Ge surfaces via the alkane chains and they are mechanically robust and electronically interlinked. Interestingly, both surface polymers and substrates retain their electrical properties based on their calculated band structures, suggesting there is little electron transfer between the surface polymers and substrates. The surface-grafted polymers and underlying substrates seem to be "independent of each other", which is an ideal model of a conductive molecular wire on a traditional semiconductor substrate.

There have been several theoretical studies on the self-assembling mechanism of alkenes on silicon surfaces to form molecular arrays, where aligned molecules are absorbed on Si surfaces but they are not interlinked.[5,27,28] Only very recently, we proposed a surface in situ polymerization reaction for self-assembled 4-hydrazinyl-3-(pyridin-4-ylmethyl)-benzaldehyde (HPyMB) molecules to produce a conductive molecular wire based on pyridines alternating adsorption on a line of exposed surface Si atoms.[29] In this work, we extended the study to thiophene-substituted alkanes self-assembling on H−Si/Ge surfaces, based on the experimental approved olefins surface self-assembling mechanism, to produce single molecular wires (surface-grafted polymers) via in situ polymerization reaction subsequently. Our work provides a new perspective on the fabrication of conductive molecular wires or polymer chains on

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Table 1. Adsorption Energy for Intermediate State (E_{ads}-1) and for the State after H-Abstraction (E_{ads}-2), Molecular Growth Activation Energy for H Extraction (E_{act}), Energy Differences between Homolateral and Heterolateral Molecular Arrays (ΔE), and the Polymerization Energy for Heterolateral (E_{hetero}) and Homolateral (E_{homo}) Structures of Thiophene Substituted Alkenes on Si(100)-2×1 and Ge(100)-2×1 Surfaces[a]

	Si(100)-2×1				Ge(100)-2×1			
n	0	1	2	3	0	1	2	3
E_{ads}-1 (eV)	0.62	0.28	0.27	0.35	0.16	0.05	0.19	0.03
E_{ads}-2 (eV)	1.06	1.19	1.16	1.12	0.98	1.11	1.13	1.10
E_{act} (eV)	0.57	0.51	0.55	0.50	0.88	0.82	0.86	0.85
ΔE (eV)	−0.05	−0.23	−0.20	−0.22	−0.06	−0.14	−0.12	−0.08
E_{hetero} (eV)	1.02	0.77	0.74	0.54	1.06	0.92	0.77	0.67
E_{homo} (eV)	1.76	1.76	1.78	1.73	1.66	1.69	1.68	1.64

[a]Schematic surface reactions can be found in Figure 2.

traditional semiconductor substrates and uncovers the mechanism of the molecular wire conductivity.

2. COMPUTATIONAL MODELS AND METHODS

We used a 2 × 2 orthogonal supercell model for both H-Si(100)2×1 and H-Ge(100)2×1 surfaces with five silicon/germanium layers. The atoms in the three bottom layers are fixed and the bottom layer is passivated with hydrogen to mimic the bulk Si/Ge. On the top surface, the Si/Ge atoms are saturated with hydrogen atoms with one H-empty site. The vacuum space is more than 10 Å. The model for H_2C═CH-$(CH_2)_n$-thiophene absorbed on the H-Si(001)2×1 surface with a C-radical is depicted in Figure 1b.

All calculations were performed within the framework of a spin-polarized plane-wave DFT implemented in the Vienna ab initio simulation package (VASP).[30,31] We adopted Perdew-Burke-Ernzerhof functional[32] for exchange-correlation, and projector augmented wave potentials[33] were used to describe the electron−ion interactions. The electronic wave functions were expanded in plane-wave basis with a cutoff energy of 400 eV. The Brillouin-zone was sampled 5 × 3 × 1 using the Γ-centered Monkhorst−Pack[34] scheme for geometry optimization and a 11 × 5 × 1 grid for band structure calculations of the polyalkylthiophene-Si/Ge(001)2×1 structure. Convergence was reached when the Hellmann−Feynman forces on each atom are less than 0.02 eV/Å.

We used the climbing-image nudged elastic band (cNEB) method[35] to locate the transition states (TS) for the H-extraction reactions of the adsorbed molecules to grow into molecular array. The calculations were performed within a 2 × 2 supercell and a k-mesh of 5 × 3 × 1 as mentioned above. Besides, vibrational calculations were performed to confirm the transition states in the molecular growth using cluster models, where fixed SiH_3/GeH_3 group was used to mimic the superlattice surfaces in supercells of 17 × 17 × 20 Å^3 (for n = 0−2) and 17 × 17 × 25 Å^3 (for n = 3), respectively [see Figure S1 in the Supporting Information (SI)]. The effect of an external electric field (EEF) was simulated via an artificial dipole sheet placed in the middle of the vacuum[36] normal to the Si/Ge(001) surfaces [Figure 1f].

3. RESULTS AND DISCUSSION

In experiments, using AFM/STM nanopatterning/lithography technologies, a selected surface hydrogen atom can be kicked off from a H-Si(001)2×1 or a H-Ge(001)2×1 surfaces [H-Si/Ge(001)2×1], to create an empty site with a Si/Ge dangling bond (DB).[2,7,37−40] A thiophene substituted ethylene, H_2C═CH-thiophene (as an example, n = 0), can bond to the H-empty site without any energy barrier and thereafter generate a C-centered radical intermediate [Figure 1b]. The adsorption is exothermic, and the calculated adsorption energies are 0.62 and 1.06 eV for intermediate state and the final state, respectively, after H-abstraction according to the following formula, E_{ads} = E[molecule] + E[surface] − E[molecule/surface]; here E[···] represents the energy of an isolated molecule [H_2C═CH-$(CH_2)_n$-thiophene], a H-Si/Ge(001)2×1 surface with a H-empty site, and the total energy of a H-Si/Ge(001)2×1 surface with an absorbed molecule, respectively. E_{ads} gives the average absorption energy of the first absorbed molecule, which is comparable to those Si surface absorption energies reported for alkenes such as styrene.[5,28] There is a variation in the adsorption energy (E_{ads}) with the length of alkene chain (n = 0−3), and thiophene substituted propylene (n = 1) has the largest adsorption energy (Table 1).

Different from the sulfur atoms in mercaptans,[8] the sulfur atoms in thiophene are inert and they are not able to bond to the H-empty sites. To clarify it, we calculated the S−Si bonding energy of a 3-allylthiophene to a surface silicon atom at a H-empty site via its thiophene sulfur atom and got the adsorption energy of 0.05 eV. In comparison, the bonding energy of an ethenyl bonding to a surface Si atom (C−Si) is about 1.0 eV. Therefore, it is not possible for thiophene sulfur instead of ethenyl group to bond to surface silicon.

Actually, we have considered all possible reactions which may occur on the surface or between the absorbed molecules, such as the second C atom of ethenyl (C═C) to absorb on surface silicon atoms, leaving the end methylene (H_2C) group as a radical. The absorption energy of second C atom to bond with the surface Si atom is about 0.1 eV which is much weaker than the first C atom with surface (see Table 1). More importantly, comparing to the first C atom, the steric obstruction is dramatically increasing for the second C atom to bond to the surface Si atom and it is kinetically unfavorable. Therefore, such absorption has not observed in experiments. The end carbon of double bond in 3-allylthiophene is the sole reactive point for the H_2C═CH-$(CH_2)_n$-thiophene molecules on aforementioned surfaces. It is also hardly for C-centered radical to abstract hydrogen across the row because the distance between the carbon radical and surface H atom cross row is about 5.3 Å. In addition, the distance between the C-centered radical and the second C of neighboring absorbed H_2C═CH-$(C_2H_2)_n$-thiophene is about 3.9 Å which is too far away, and the polymerization reaction cannot occur between them. Because a radical is very reactive, there should be some side reactions

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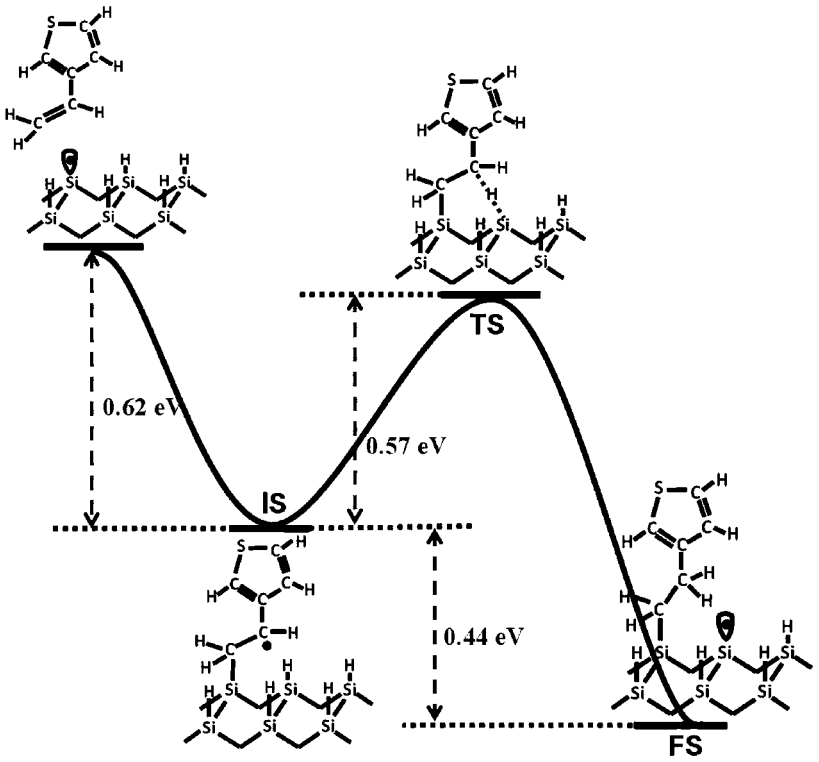

Figure 2. Energy profile of a thiophene substituted ethane (n = 0) growth reaction on H-Si(001)2×1 surface. Schematic structures of the initial state (IS), transition state (TS), and final state (FS) of the H-abstracting process are given.

which can terminate the 1D growth reaction. This is another topic, and we may consider that in our future work.

To study the growth of the molecular array, we calculated the activation energy for a C-centered radical intermediate [Figure 1b] to extract one H atom from the adjacent surface silicon atom in the neighboring Si dimer. The energy profile of a thiophene substituted ethylene (n = 0) growth reaction on a H−Si(001)2×1 surface is depicted in Figure 2. The initial adsorption of a H_2C═CH-thiophene on a H-empty site, where a Si dangling bond is present, is spontaneous with the initial adsorption energy of 0.62 eV, which results in the formation of a C−Si bond after the breaking of the ethylene C−C π-bond. Subsequently, a C-centered radical is formed, that is a very reactive intermediate state (IS) and will abstract one H atom from the adjacent Si atom to saturate itself forming ethane. The calculated energy barrier for this process is 0.57 eV, which is lower than the initial adsorption energy and much lower than the adsorption energy (1.06 eV, after H abstraction from the neighboring Si site). We therefore can expect that the initial state is able to trespass the transition state (TS) to reach the final state (FS) quite easily and simultaneously create a new H-empty site for the next molecular absorption. As this process continues, a thiophene substituted ethane molecular array is formed on the silicon surface eventually. The absorption and activation energies for the reaction of H_2C═CH-$(CH_2)_n$-thiophene on H-Si(001)2×1 are comparable to olefins grown on silicon surface reported previously. For example, styrene has been proven to be able to absorb and self-grow into 1D molecular array on H-Si(001)2×1 following the same scenario. The activation energy of growth, i.e., H-abstraction, is 0.88 eV based on the DFT calculations done by Jun-Hyung Cho et al.[5] and later modified to 0.52 eV in 2011.[28] The H-abstraction energy for H_2C═CH-$(CH_2)_n$-thiophene is around 0.50 to ~0.57 eV much lower than absorption energies (Table 1), meaning that thiophene substituted alkenes are feasible and easy to self-grow into a 1D molecular array on the Si surface. Moreover, we found that the surface adsorption energies for the same molecules on H−Ge(001)2×1 are slightly lower than that on H−Si(001)2×1 due to weaker Ge−C bond energy than that of C−Si, but the molecular growth activation energies are much higher (Table 1). This observation indicates that the thiophene-alkenes are harder to grow on the H-Ge(001)2×1 surface. The reason is mainly due to the higher electronegativity of Si atoms than Ge atoms, and the surface H−Si bonds are more polar than H−Ge, so that positively charged H atoms in the Si surface are easily attracted by the negatively charged C-centered radical intermediate. Meanwhile, surface Ge atoms are farther away from each other than surface Si atoms, elevating the growth energy of TS on the Ge surface. Therefore, in the following discussion, we focus mainly on the H-Si(001)2×1.

We are also noted that H abstraction may occur from the same Si dimer; therefore we calculated the energy barrier of H abstraction from the same Si dimer for n = 0. The calculated energy barrier is 0.80 eV, which is much higher than 0.57 eV for H abstraction from the neighboring Si dimer, indicating that the radical chain reaction along the [011] direction is more favorable and predominant. Furthermore, high energy barrier of 0.80 eV implies the H abstraction from the same Si dimer could occur at higher temperatures, which is in accordance with an experimentally observed double-line molecular array for styrene.[3] We may consider such two-direction growth in our future work.

We next studied the effect of alkene chain length on molecular array growth. It is found that the chain length only shows a weak effect on the activation energies (E_{act}) in which longer chains show only a slightly lower E_{act}. In addition, based

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on the cluster models mentioned above, we performed transition states (TS) vibrational mode calculations for all eight reactions (four on silicon and four on germanium surfaces). The results show only one soft mode with imaginary frequency for each of the transition state in H-extraction reaction. Each eigenvector of the soft mode corresponds to the motion of H atom on Si/Ge surfaces toward the C-centered radical (Figure S2 in SI), confirming that the TSs are identified correctly.

Actually, when the molecules grow on surfaces, the newly formed molecular arrays can bend to different directions, thereafter forming different configurations. Here, we are focusing on two specific configurations, namely homolateral and heterolateral structures with respect to the [011] direction on the Si surface [Figure 1c,d]. The homolateral structure refers to the one that all alkanes absorb on the surface in parallel, while the heterolateral structure is the one that the adjacent absorbed alkanes bend to opposite directions. As expected, the heterolateral structures are more stable, and the energy difference between the homolateral and heterolateral structures becomes larger with the increase in the alkane chain length (n). This is because the increased degree of freedom in longer alkane chains reduces the intramolecular and intermolecular repulsion (Table 1). To study the intermolecular interactions, we calculated the average adsorption energies after first, second, and third $H_2C{=}CH\text{-}(CH_2)_n$-thiophene adsorptions and molecular array formations for heterolateral configuration when n = 0−3 on silicon surface using 4 × 2 supercell, and the results are given in Table S1 in the Supporting Information. The values of the average adsorption energies after first, second, third are very close, meaning that the intermolecular interactions between adsorbed molecules are not prominent. The average adsorption energies of molecular arrays are slightly lower than that after third isolated molecule.

It is noted that in both heterolateral and homolateral structures, the thiophene rings are situated side by side at the top end of the molecular array. Considering longer alkane chains may have more possible conformations, we did not consider the cases for n > 3. Using nanopatterning technologies in surface science, radicals can be created on a surface adsorbed molecule using AFM or STM tips or even UV light. Once a radical is introduced onto one of the thiophene rings, an in situ polymerization reaction occurs spontaneously, forming polyalkylthiophene/Si/Ge(100)2×1, a surface grafted single-line polymer structure, as in most radical polymerization reactions.

Nowadays, there have been a few examples on surface grafting control reactions using AFM tips or UV light activations. Goda et al. reported a biomimetic phosphorylcholine polymer grafting from polydimethylsiloxane surface using photoinduced polymerization.[41] Lisboa et al. deposited polypyrrole (PPy) films done by grafting allylamine or acrylic acid using UV light radical activation.[42] Radical-introducing essentially increases the internal energy of the molecules and allows them to overcome the energy barriers for polymerization. However, due to the space constraints, the newly formed polythiophene cannot be perfectly coplanar [Figures 1e,f and 3]. The polymerization is an endothermic process, and the relevant heats/energies needed are listed in Table 1. It is seen that the energies required for the heterolateral structure are much lower than that for homolateral, and decrease along with increasing n, the chain length of alkanes. This is because longer chains relieve the tensions in the polymer structures and, hence, enable polythiophene to be more coplanar. Figure 3

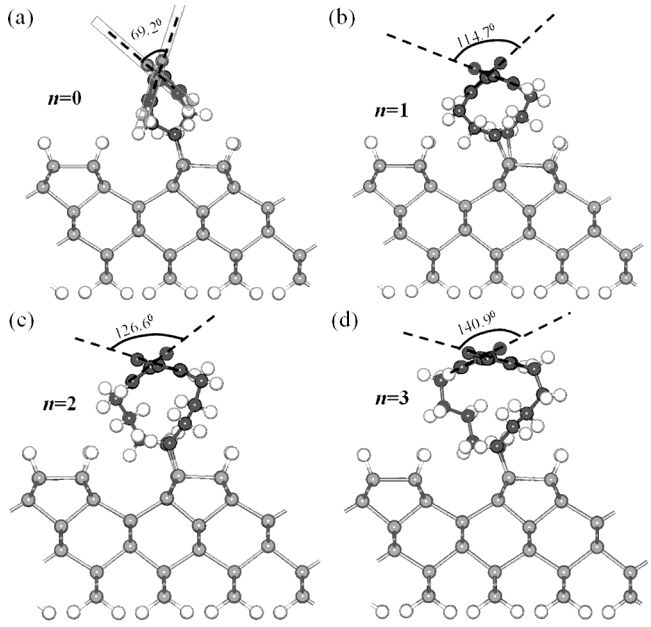

Figure 3. Dihedral angles between two adjacent thiophene rings in heterolateral polyalkylthiophenes on H-Si(100)2×1 surface for different lengths (n) of substituted alkene.

shows the dihedral angles between two adjacent thiophene rings in different polyalkylthiophenes on silicon surfaces. Indeed, the more coplanar the thiophene rings, the lower the energy required. It must be noted that all these polymerization energies are lower than the adsorption energy, and for polypentylthiophene (n = 3), E_{hetero} is even less than half of E_{ads}. We will elucidate the heterolateral polythiophenes properties in the remaining section.

The aforementioned in situ polymerization reactions are irreversible. The newly formed polyalkylthiophenes are chemically bonded to the Si/Ge surfaces via the alkanes, which is different from the polythiophenes growth on Cu crystal surfaces.[24,25] To study their electronic properties, we calculated the band structures of polyalkylthiophenes on H-Si/Ge(100)2×1. Larger band gaps (Δ) are found on silicon than on germanium surfaces and the band gap decreases with an increase in the alkane length (Table 2). Comparing the band

Table 2. Band Gaps (Δ) for Polyalkylthiophenes on H-Si(100)2×1 and H-Ge(100)2×1 Surfaces, Respectively, and Δ Values under a 0.2 V/Å External Electric Field (EEF) Normal to the Surfaces

	Si(100)-2×1		Ge(100)-2×1	
n	Δ (eV)	Δ (eV) at EEF = 0.2 V/Å	Δ (eV)	Δ (eV) at EEF = 0.2 V/Å
0	1.28	0.97	0.87	0.86
1	1.27	0.89	0.87	0.67
2	1.12	0.53	0.86	0.65
3	0.92	0.27	0.86	0.39

structure of the pristine H-Si(100)2×1, we found the surface polymers did not obviously affect the substrate band structures by only shifting the Fermi level [Figure 4a−d]. This observation indicates little electron transfer between polyalkylthiophene chains and the substrates. Although the surface-grafted polymers are chemical bonded to the surfaces, both

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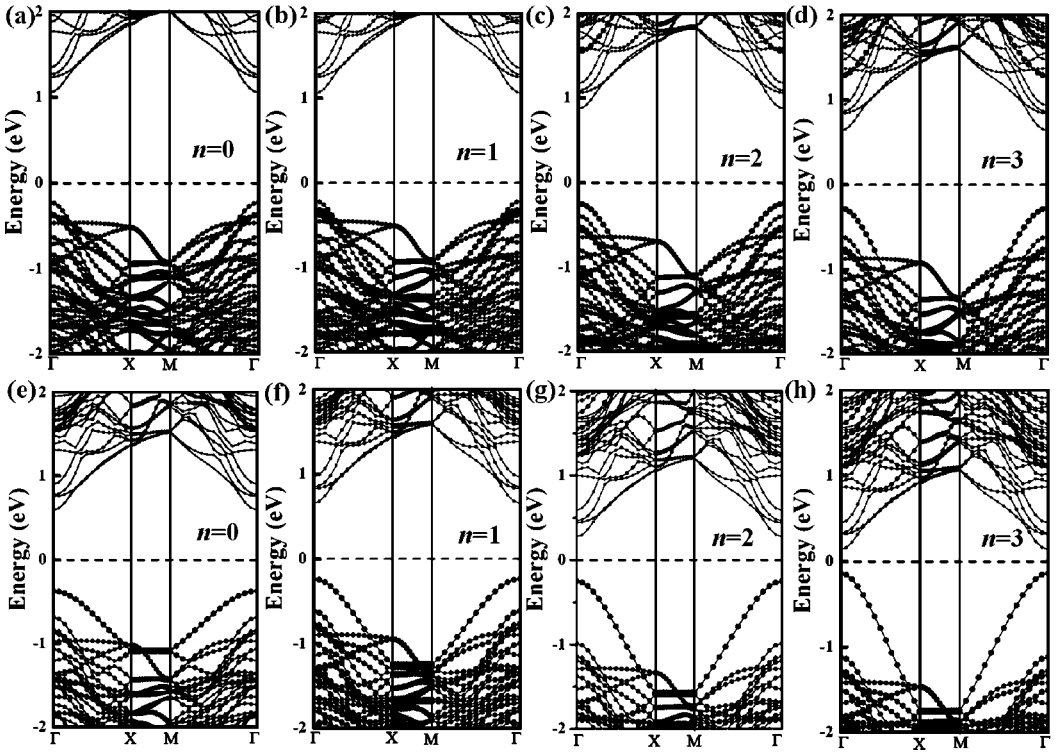

Figure 4. (a–d) Band structures of the polyalkylthiophenes/Si(100)2×1 and (e–h) band structures under EEF at 0.2 V/Å. Red and black circles represent the components of polyalkylthiophenes and silicon substrate, respectively. The size of the circles denotes the contributions from different components.

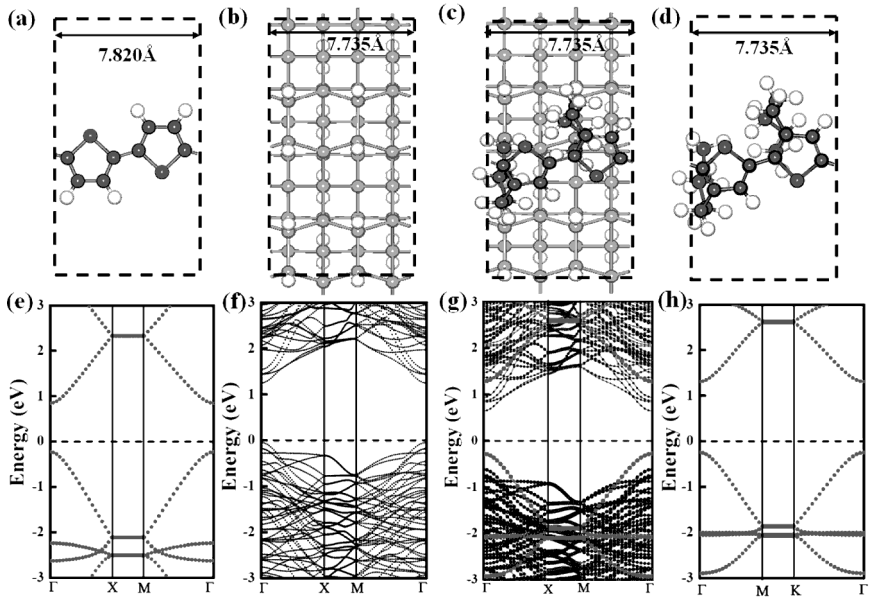

Figure 5. (a) Optimized structure of pure polythiophene chain and (e) its band structure; (b) H-Si(001)2×1 structure and (f) its band structure; (c) a polypentylthiophene/Si(001)2×1 surface-grafted polymer and (g) its band structure; (d) a pure organic polypentylthiophene chain and (h) its band structure. Red and black dots are the components of organic molecules and inorganic substrate, respectively.

polymers and substrates seem to retain their original electron structures and exhibit independent electronic properties, which actually are ideal for molecular wires on semiconductor substrates.

This unique feature is further confirmed by comparing the band structures of (1) a single perfect polythiophene chain (the dihedral angles between adjacent thiophene rings, θ = 180°), (2) a perfect H-Si(100)2×1 surface, (3) polypentylthiophene/Si(001)2×1 structure, and (4) the polypentylthiophene chain after removing the silicon substrate (Figure 5). Interestingly, the band structure (3) resembles the combination of (2) and (4), indicating the intrinsic electronic structures of surface polymers and the substrates changed little. At the same time, the band structures of (1) and (4) look very similar; implying the properties of the surface polypentylthiophene chain should be close to that of the perfect coplanar polythiophene.

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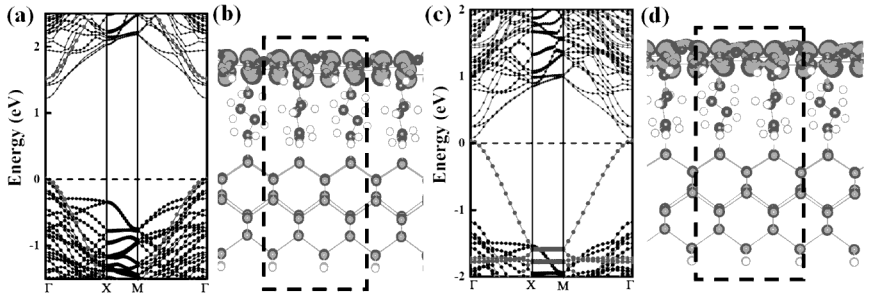

Figure 6. (a) Band structure of polypentylthiophene/Si(001)2×1 after removing 0.1 electrons; (b) isodensity surface of the band crossing Fermi level in (a); (c) band structure of polypentylthiophene/Si(001)2×1 under EEF of 0.3 V/Å; and (d) isodensity surface of the conductive band which cross Fermi level in (c).

Similar to other conductive polymers, these surface-grafted single-line polyalkylthiophenes are semiconductors in the natural state according to their band structures given in Figures 4 and 5. In real application, the polymers must be linked between two electrodes with applied electrical voltages, where electrons/holes are injected into the conductive polymers. It must be pointed out that polyalkylthiophenes/Si(001)2×1 structures are the real conductive molecular wire on the silicon surfaces only when the polythiophene chains are confirmed as the sole conductive channels. Thereafter, various electron/hole amounts doping into the polyalkylthiophenes/Si(001)2×1 structures were studied. It was found that, for example, 0.1 hole doping per unit can make the polypentylthiophene/Si(001)2×1 conductive [Figure 6a]. Furthermore, we have identified the conductive band and calculated the electronic isodensity surface, showing it confined within the polypentylthiophene chain [Figure 6b]. Applying an EEF is an alternative way to fine-tune the electrical properties of the polyalkylthiophenes/Si(001)2×1. The band structures calculated under an EEF of 0.2 V/Å normal to the silicon surface are shown in Figure 4e–h. It is clear that EEF narrows the band gaps; and polypentylthiophene/Si(001)2×1 becomes conductive at 0.3 V/Å [Figure 6c]. Again, we have confirmed the polythiophene chain is the sole conductive channel in this surface-grafted polymer structure [Figure 6d].

4. CONCLUSIONS

In this work, we have studied self-assembled growth of a series of homologue, $H_2C{=}CH\text{-}(CH_2)_n$-thiophene ($n$ = 0–3) and the in situ polymerization on H-Si(100) and H-Ge(100) surfaces based on DFT calculations. According to the reaction energy profiles, we proved that $H_2C{=}CH\text{-}(CH_2)_n$-thiophene can grow into 1D molecular arrays because the growing activation energies are much lower than the adsorption energies, especially on the silicon surfaces. Furthermore, irreversible in situ polymerization reactions can occur within the thiophene rings located at the end top of the molecular arrays once radicals are introduced into the thiophene rings, forming polyalkylthiophenes/Si(001)2×1. These single polymeric chains are chemically bonded to the surfaces via strong covalent bonds and could be classified as a surface-grafted polymer. Interestingly, both polymers and substrates retain their own major electronic characteristics. In addition, these surface polymers can be made conductive by hole doping or applying an external electric field. More importantly, the polythiophene chain is the sole conductive channel in the system. Our finding provides a theoretical guide to fabricate ideal molecular wires on traditional semiconducting surfaces, which could find potential applications in molecular electronic devices.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b08389.

Cluster model used for transition state location (Figure S1), the soft mode corresponding to the transition state (Figure S2), and the adsorption energies for molecular arrays (Table S1). (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Binnig, G.; Rohrer, H.; Gerber, C.; Weibel, E. 7 × 7 Reconstruction on Si(111) Resolved in Real Space. *Phys. Rev. Lett.* **1983**, *50*, 120–123.

(2) Shedd, G. M.; Russell, P. E. The Scanning Tunneling Microscope as a Tool for Nanofabrication. *Nanotechnology* **1990**, *1*, 67–80.

(3) Lopinski, G. P.; Wayner, D. D. M.; Wolkow, R. A. Self-Directed Growth of Molecular Nanostructures on Silicon. *Nature* **2000**, *406*, 48–51.

(4) Piva, P. G.; DiLabio, G. A.; Pitters, J. L.; Zikovsky, J.; Rezeq, M.; Dogel, S.; Hofer, W. A.; Wolkow, R. A. Field Regulation of Single-Molecule Conductivity by a Charged Surface Atom. *Nature* **2005**, *435*, 658–661.

(5) Cho, J.; Oh, D.; Kleinman, L. One-Dimensional Molecular Wire on Hydrogenated Si(001). *Phys. Rev. B: Condens. Matter Mater. Phys.* **2002**, *65*, 081310.

(6) Kruse, P.; Johnson, E. R.; DiLabio, G. A.; Wolkow, R. A. Patterning of Vinylferrocene on H-Si(100) via Self-Directed Growth of Molecular Lines and STM-Induced Decomposition. *Nano Lett.* **2002**, *2*, 807–810.

(7) Basu, R.; Guisinger, N. P.; Greene, M. E.; Hersam, M. C. Room Temperature Nanofabrication of Atomically Registered Heteromolec-

DOI: 10.1021/acs.jpcc.6b08389
J. Phys. Chem. C 2016, 120, 25612–25619

ular Organosilicon Nanostructures Using Multistep Feedback Controlled Lithography. *Appl. Phys. Lett.* **2004**, *85*, 2619.
(8) Hossain, M. Z.; Kato, H. S.; Kawai, M. Controlled Fabrication of 1D Molecular Lines Across the Dimer Rows on the Si(100)-(2×1)-H Surface through the Radical Chain Reaction. *J. Am. Chem. Soc.* **2005**, *127*, 15030−15031.
(9) DiLabio, G. A.; Piva, P. G.; Kruse, P.; Wolkow, R. A. Dispersion Interactions Enable the Self-Directed Growth of Linear Alkane Nanostructures Covalently Bound to Silicon. *J. Am. Chem. Soc.* **2004**, *126*, 16048−16050.
(10) Pitters, J. L.; Dogel, I.; DiLabio, G. A.; Wolkow, R. A. Linear Nanostructure Formation of Aldehydes by Self-Directed Growth on Hydrogen-Terminated Silicon(100). *J. Phys. Chem. B* **2006**, *110*, 2159−2163.
(11) Walsh, M. A.; Walter, S. R.; Bevan, K. H.; Geiger, F. M.; Hersam, M. C. Phenylacetylene One-Dimensional Nanostructures on the Si(100)-2×1:H Surface. *J. Am. Chem. Soc.* **2010**, *132*, 3013−3019.
(12) Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. Catalyst-Transfer Polycondensation. Mechanism of Ni-Catalyzed Chain-Growth Polymerization Leading to Well-Defined Poly(3-Hexylthiophene). *J. Am. Chem. Soc.* **2005**, *127*, 17542−17547.
(13) Günes, S.; Neugebauer, H.; Sariciftci, N. S. Conjugated Polymer-Based Organic Solar Cells. *Chem. Rev.* **2007**, *107*, 1324−1338.
(14) Reyes-Reyes, M.; Kim, K.; Carroll, D. L. High-Efficiency Photovoltaic Devices Based on Annealed Poly(3-Hexylthiophene) and 1-(3-Methoxycarbonyl)-Propyl-1- Phenyl-(6,6)C61 Blends. *Appl. Phys. Lett.* **2005**, *87*, 083506.
(15) Sista, P.; Ghosh, K.; Martinez, J. S.; Rocha, R. C. Polythiophenes in Biological Applications. *J. Nanosci. Nanotechnol.* **2014**, *14*, 250−272.
(16) Sirringhaus, H.; Brown, P. J.; Friend, R. H.; Nielsen, M. M.; Bechgaard, K.; Langeveld-Voss, B. M. W.; Spiering, A. J. H.; Janssen, R. A. J.; Meijer, E. W.; Herwig, P.; et al. Two-Dimensional Charge Transport in Self-Organized, High-Mobility Conjugated Polymers. *Nature* **1999**, *401*, 685−688.
(17) Iovu, M. C.; Jeffries-EL, M.; Sheina, E. E.; Cooper, J. R.; McCullough, R. D. Regioregular Poly(3-Alkylthiophene) Conducting Block Copolymers. *Polymer* **2005**, *46*, 8582−8586.
(18) Bao, Z.; Lovinger, A. J. Soluble Regioregular Polythiophene Derivatives as Semiconducting Materials for Field-Effect Transistors. *Chem. Mater.* **1999**, *11*, 2607−2612.
(19) Yang, L.; Sontag, S. K.; LaJoie, T. W.; Li, W.; Huddleston, N. E.; Locklin, J.; You, W. Surface-Initiated Poly(3-Methylthiophene) as a Hole-Transport Layer for Polymer Solar Cells with High Performance. *ACS Appl. Mater. Interfaces* **2012**, *4*, 5069−5073.
(20) Doubina, N.; Jenkins, J. L.; Paniagua, S. A.; Mazzio, K. A.; MacDonald, G. A.; Jen, A. K. Y.; Armstrong, N. R.; Marder, S. R.; Luscombe, C. K. Surface-Initiated Synthesis of Poly(3-Methylthiophene) from Indium Tin Oxide and its Electrochemical Properties. *Langmuir* **2012**, *28*, 1900−1908.
(21) McCullough, R. D. The Chemistry of Conducting Polythiophenes. *Adv. Mater.* **1998**, *10*, 93−116.
(22) Ma, W.; Yang, C.; Gong, X.; Lee, K.; Heeger, A. J. Thermally Stable, Efficient Polymer Solar Cells with Nanoscale Control of the Interpenetrating Network Morphology. *Adv. Funct. Mater.* **2005**, *15*, 1617−1622.
(23) Sakaguchi, H.; Matsumura, H.; Gong, H.; Abouelwafa, A. M.; Abouelwafa, A. M. Direct Visualization of the Formation of Single-Molecule Conjugated Copolymers. *Science* **2005**, *310*, 1002−1006.
(24) Sakaguchi, H.; Matsumura, H.; Gong, H. Electrochemical Epitaxial Polymerization of Single-Molecular Wires. *Nat. Mater.* **2004**, *3*, 551−557.
(25) Lipton-Duffin, J. A.; Miwa, J. A.; Kondratenko, M.; Cicoira, F.; Sumpter, B. G.; Meunier, V.; Perepichka, D. F.; Rosei, F. Step-By-Step Growth of Epitaxially Aligned Polythiophene by Surface-Confined Reaction. *Proc. Natl. Acad. Sci. U. S. A.* **2010**, *107*, 11200−11204.
(26) Lipton-Duffin, J. A.; Ivasenko, O.; Perepichka, D. F.; Rosei, F. Synthesis of Polyphenylene Molecular Wires by Surface-Confined Polymerization. *Small* **2009**, *5*, 592−597.
(27) Kang, J. K.; Musgrave, C. B. A Quantum Chemical Study of the Self-Directed Growth Mechanism of Styrene and Propylene Molecular Nanowires on the Silicon (100) 2×1 Surface. *J. Chem. Phys.* **2002**, *116*, 9907−9913.
(28) Lee, J.; Choi, J.; Cho, J. Enhanced Stability and Electronic Structure of Phenylacetylene Lines on the Si(100)-(2×1):H Surface. *J. Phys. Chem. C* **2011**, *115*, 14942−14946.
(29) Yao, X.; Wang, J.; Yuan, S.; Zhang, X.; Wu, G.; Wang, X.; Yang, S. A Theoretical Guide for Fabricating a Conductive Molecular Wire on a Silicon Surface via an *in situ* Surface Polymerization Reaction. *Nanoscale* **2015**, *7*, 15277−15283.
(30) Kresse, G.; Hafner, J. Ab Initio Molecular Dynamics for Open-Shell Transition Metals. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1993**, *48*, 13115−13118.
(31) Kresse, G.; Furthmüller, J. Efficiency of Ab-Initio Total Energy Calculations for Metals and Semiconductors Using a Plane-Wave Basis Set. *Comput. Mater. Sci.* **1996**, *6*, 15−50.
(32) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865−3868.
(33) Blochl, P. E. Projector Augmented-Wave Method. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1994**, *50*, 17953−17979.
(34) Monkhorst, H. J.; Pack, J. D. Special Points for Brillonin-zone Integrations. *Phys. Rev. B* **1976**, *13*, 5188−5192.
(35) Henkelman, G.; Uberuaga, B. P.; Jónsson, H. A Climbing Image Nudged Elastic Band Method for Finding Saddle Points and Minimum Energy Paths. *J. Chem. Phys.* **2000**, *113*, 9901−9904.
(36) Neugebauer, J.; Scheffler, M. Adsorbate-Substrate and Adsorbate-Adsorbate Interactions of Na and K Adlayers on Al(111). *Phys. Rev. B: Condens. Matter Mater. Phys.* **1992**, *46*, 16067−16080.
(37) Abeln, G. C.; Hersam, M. C.; Thompson, D. S.; Hwang, S. T.; Choi, H.; Moore, J. S.; Lyding, J. W. Approaches to Nanofabrication on Si(100) Surfaces: Selective Area Chemical Vapor Deposition of Metals and Selective Chemisorption of Organic Molecules. *J. Vac. Sci. Technol., B: Microelectron. Process. Phenom.* **1998**, *16*, 3874−3878.
(38) Walsh, M. A.; Hersam, M. C. Atomic-Scale Templates Patterned by Ultrahigh Vacuum Scanning Tunneling Microscopy on Silicon. *Annu. Rev. Phys. Chem.* **2009**, *60*, 193−216.
(39) Hersam, M. C.; Guisinger, N. P.; Lyding, J. W. Isolating, Imaging, and Electrically Characterizing Individual Organic Molecules on the Si(100) Surface with the Scanning Tunneling Microscope. *J. Vac. Sci. Technol., A* **2000**, *18*, 1349−1353.
(40) Abeln, G. C.; Lee, S. Y.; Lyding, J. W.; Thompson, D. S.; Moore, J. S. Nanopatterning Organic Monolayers on Si(100) by Selective Chemisorption of Norbornadiene. *Appl. Phys. Lett.* **1997**, *70*, 2747−2749.
(41) Goda, T.; Konno, T.; Takai, M.; Moro, T.; Ishihara, K. Biomimetic Phosphorylcholine Polymer Grafting From Polydimethylsiloxane Surface Using Photo-Induced Polymerization. *Biomaterials* **2006**, *27*, 5151−5160.
(42) Lisboa, P.; Gilliland, D.; Ceccone, G.; Valsesia, A.; Rossi, F. Surface Functionalisation of Polypyrrole Films Using UV Light Induced Radical Activation. *Appl. Surf. Sci.* **2006**, *252*, 4397−4401.

DOI: 10.1021/acs.jpcc.6b08389
J. Phys. Chem. C 2016, 120, 25612−25619