

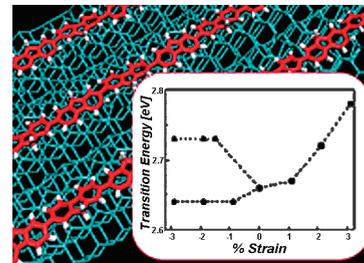
# Uniaxial Strain in Molecular Nanowires: A Case Study of $\beta$ -phase Polyfluorenes

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**ABSTRACT** The response of flexible organic semiconducting fluorene nanowires to structural manipulation and adsorption-induced uniaxial strain is investigated using first-principles methods. In agreement with experiments, the calculated shifts in transition energies of strained planar fluorenes do not lead to a molecular phase change but are modified according to whether deformations promote or suppress conjugation along the backbone. We identify two energetically identical modes for compressing the molecule, which cause shifts in opposite directions, depending on the impact of the deformation on the strength of conjugation. We also consider surface adsorption as a practical means for inducing strain. Although the polymer can be linearly extended through mismatch with the surface lattice, properties are likely to be dominated by local compressed regions.

**SECTION** Nanoparticles and Nanostructures



The mechanical flexibility of organic semiconductors is a material feature which makes them attractive for incorporation in electronic devices. Understanding the relationship between their optoelectronic properties and structure at the molecular level has, however, remained a challenge on account of the complexity of competing inter- and intramolecular interactions. In addition to chemical composition, directed strain is a further means for manipulating the optoelectronic properties of organics, but practically, it is harder to find ways to apply specific strain to a “soft” organic film and especially a single molecule. Strain has been identified as playing a major role in determining the configuration of polyfluorenes, where three phases have been characterized according to the degree of order between monomers. Ordered  $\beta$ -phase polyfluorenes,<sup>1</sup> in which fluorene monomers are aligned within the same plane, are stable when the molecule is elongated along the molecular axis (Figure 1). This configuration is observed both in thin films<sup>2–4</sup> and on the single-molecule level.<sup>5</sup> The translational symmetry along the molecular axis permits single molecules to be viewed as flexible nanowires. These nanowires have been found to be stable experimentally with regards to uniaxial strain, where bent molecules have the same fluorescence frequency but with a broader line width than linear configurations.<sup>6</sup> The response of isolated gas-phase oligomers to uniaxial strain can readily be determined using first-principles quantum chemistry techniques. Previous theoretical studies have considered how the distribution of strain in molecular structural parameters in polyacetylene and polyethylene<sup>7</sup> and charge transfer in polyacetylene<sup>8</sup> affect the Young’s modulus of the molecules using semiempirical-based methods for a microscopic description of the elasticity of bulk materials. In this study, we compute and compare the molecular response to uniaxial strain of planar fluorenes, which we discuss in light of

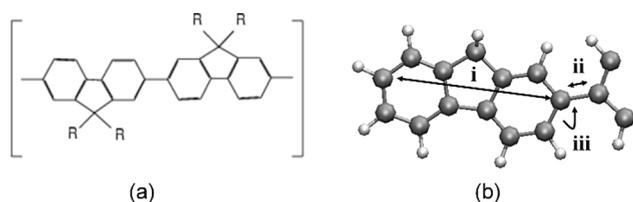
experiments on bent isolated molecules.<sup>6</sup> Our calculations enable us to distinguish between strain stored in structural parameters and in morphology changes and determine how the strength of conjugation is affected by calculating the vertical transition energies. Energetic shifts can thus be associated with mechanical constraints, caused, for instance, by interactions with the experimental environment.

For practical situations, a means of inducing uniaxial strain in the backbone is required, and for this purpose, we consider specific adsorption on a substrate. The influence of substrate structures on the molecular configurations has been examined in the epitaxial growth of semiconducting organic molecular films where van der Waals forces are usually the predominant means of interaction between adsorbate and substrate.<sup>9,10</sup> Subsequent organic layers can readily relax to accommodate strain induced by weak interactions with the substrate. In our system, though, we emulate the principle of strain engineering in inorganic crystal structures by forming covalent bonds between substrate and adsorbate and thereby inhibit relaxation of the molecular structure. The Si(100) substrate consists of a surface layer of rows of buckled Si dimers, in which the upper dimer atom has a slight negative charge and the lower atom a slight positive charge.<sup>11</sup> Since the first demonstration that the unsaturated hydrocarbon molecule ethylene could adsorb via a cycloaddition reaction in which two Si–C  $\sigma$  bonds are formed,<sup>12,13</sup> other small unsaturated hydrocarbons have been attached to the Si(100) substrate.<sup>14,15</sup> In the case of aromatic molecules, at low coverages, experimental and computational studies show

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**Figure 1.** (a) A schematic representation of  $\beta$ -phase polyfluorene. (b) Structural parameters referred to in the text: (i) the length of the monomer, (ii) the linking bond length, and (iii) the angle between monomers.

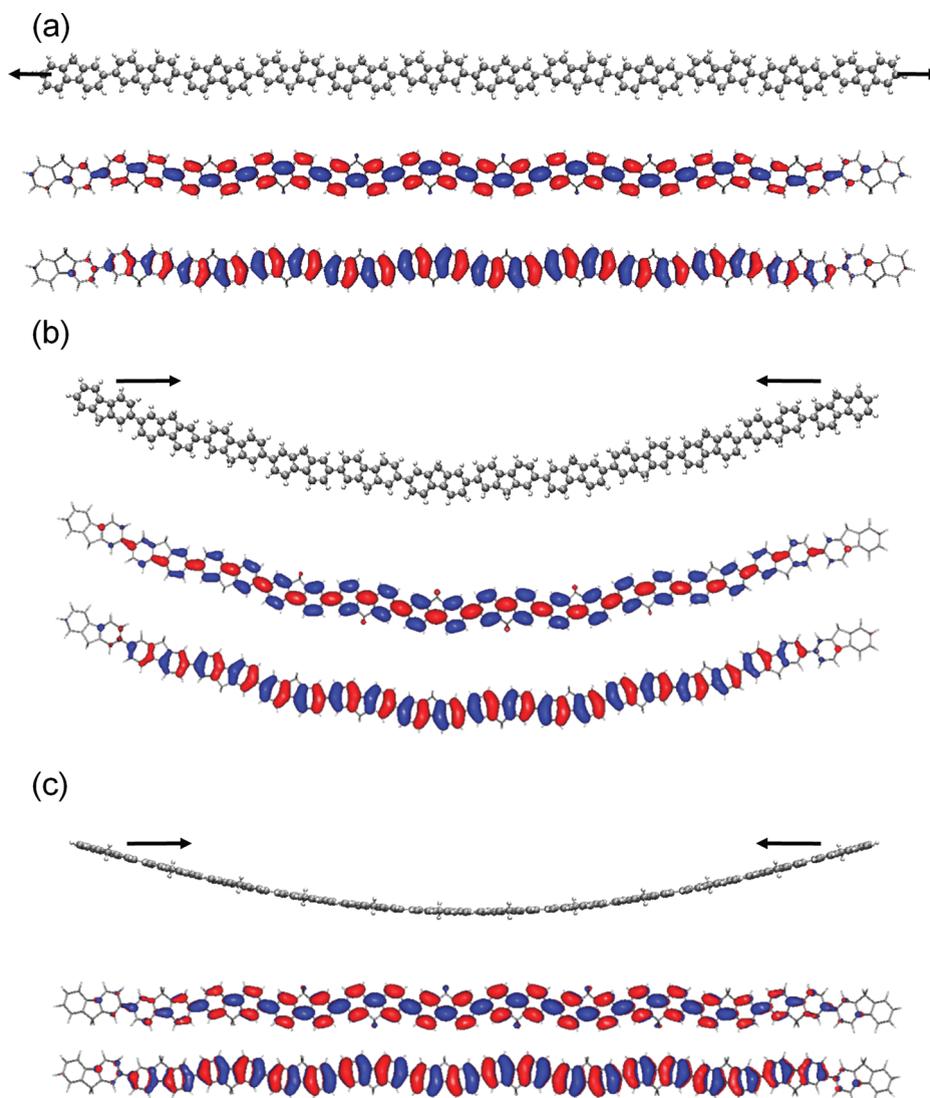
that they can adsorb intact with the molecular plane parallel to the surface plane, and distortions of the planar aromatic molecules occur as Si–C bonds are formed, breaking the aromaticity of the molecules.<sup>16–24</sup> In particular, one of the stable configurations of pentacene adsorbed on a Si(100) substrate has its molecular axis parallel to the Si dimer rows.<sup>22–24</sup> We propose the adsorption of  $\beta$ -phase polyfluorene with its molecular plane parallel to a silicon dimer row as a model system for inducing uniaxial strain in the backbone. The flexibility permitted in the backbone, resulting from the C–C bonds linking fluorene units, could potentially enable bonding over the extent of the polymer. The difference between the length of the polymer repeat unit and a certain number of Si dimer spacings can induce tensile strain in the backbone, but the distribution of strain depends on the particular alignment with the substrate. Combining our calculations on isolated molecules and molecular adsorption, we highlight how strain is distributed through the molecular backbone, while maintaining conformational order, and the potential impact this has on molecular optical properties.

The isolated linear  $\beta$ -phase fluorene dodecamer was strained by elongation and compression along the molecular axis by incremental adjustment of the distance between terminal carbon atoms. The overall morphology of the backbone does not change under tension, but compression can result either in a deformation in which the backbone is bent within or in arches out of the molecular plane, although dihedral order is maintained between fluorene units (Figure 2). There are three molecular parameters shown in Figure 1 which are distorted when the molecule is strained, the lengths of the C–C bonds linking fluorene units, the lengths of the fluorene units themselves, and the bond angles between units which determine the linearity of the molecule. The changes in bond lengths and the lengths of the monomers for a 3% strain are given in Table 1. As the angles do not change appreciably ( $< 2^\circ$ ), we do not consider them in our analysis. We determine that for 3% tensile stretching, the lengths of both the fluorene monomer and the C–C bond linking monomer units increase. For bending, the bond linking monomers decrease by 0.01 Å, and the monomer unit is slightly compressed. For arching, the linking bond does not change, but the length of the fluorene unit decreases, which is due to arching of the monomer itself as opposed to a decrease in bond lengths. Therefore, the strain is distributed over the entire molecule as it is stretched, whereas in compression, a reduction in the distance between terminal C atoms does not necessarily result in a uniform decrease of the bond parameters. In particular, compression leads to a change

in morphology which does not simply decrease bond lengths. The energetic cost for deformation, shown in Figure 3a, increases exponentially as the molecule is stretched, with an increase of 4.4 eV for 3% strain, although the energetic cost for elongation under 1% is negligible. For the modes of compression, the energetic cost is the same for both deformations, and no further change in deformation energy is observed after the initial morphology adjustment upon increasing strain. Therefore, whereas tensile stretching elongates the molecule, compression results in a significant change in the backbone morphology, which can take one of two energetically degenerate forms.

The vertical transition energies corresponding to the deformed structures (Figure 3b) show that there is a blue shift for tensile stretching (3%: 0.12 eV), a red shift for compressive bending (3%: 0.02 eV), but a blue shift for compressive arching (3%: 0.07 eV) compared to the unstrained  $\beta$ -phase dodecamer. The two modes of compression therefore have shifts in opposite directions, although the form and extent of the frontier orbitals involved in the transition, which is the lowest-energy transition and has the greatest oscillator strength, are not affected by the deformations (Figure 2). For tensile stretching, the transition energies increase with increasing strain, which corresponds to a weakening of conjugation as the bond lengths increase. For compressive bending, there is no further shift after the initial deformation, and the red shift can be understood in terms of stronger interactions as bond lengths are compressed. The transition energy corresponding to the arching deformation also does not shift further after the initial morphology change but is blue-shifted as individual fluorene units are arched, breaking the planarity of the molecule. As shown in Figure 2, there is no significant change in the extent of the frontier orbitals involved in the transition, the oligomers remain in the  $\beta$ -phase, and shifts are a result of minor changes in the structural parameters. The shifts can be qualitatively understood as being caused by a weakening of the conjugation along the backbone upon stretching and arching and by a strengthening upon bending. The effect of uniaxial strain on the vertical transition energies is therefore determined by the mode of molecular deformation in response to strain and can be understood in terms of how changes in the structural parameters affect the strength of conjugation along the backbone. As the deformation energies of the two compressed structures are practically identical, control of the direction of the shift is likely to require precise external manipulation.

We investigate a model system consisting of a  $\beta$ -phase polyfluorene adsorbed with its axis parallel to the surface dimer rows of a Si(100) substrate for inducing uniaxial strain. We combine four monomer units with nine Si surface dimers in the supercell, so that if adsorption occurs, the polymer should be extended as the cell containing the nine Si dimers is 1.2 Å longer than four molecular monomers. We determine that the polymer adsorbs intact in our system in an almost planar configuration lying 2 Å above the substrate (Figure 4). The calculated adsorption energy for the system in the calculation supercell is  $-220.23$  eV, determined according to  $E_{\text{ads.}} = E_{\text{total}} - E_{\text{surface}} - E_{\text{molecule}}$ . We note that although no instance of hydrogen transfer from the molecule to the



**Figure 2.** The strained molecular structures and HOMO (below) and LUMO (above) frontier orbitals of the  $\beta$ -phase fluorene dodecamer. The figure shows deformations for 3% strain, and the arrows indicate the direction of application of strain. The structure of the undistorted molecule (not shown) is indistinguishable from the stretched molecule. (a) The elongated molecule. (b) The compressed molecule bent in the plane of the molecule. (c) A side view of the compressed molecule arched out of the plane of the molecule; the frontier orbitals are shown in the plane from the same perspective as (a) and (b). There is no indication that the distortions have a significant impact on the extent of the orbitals.

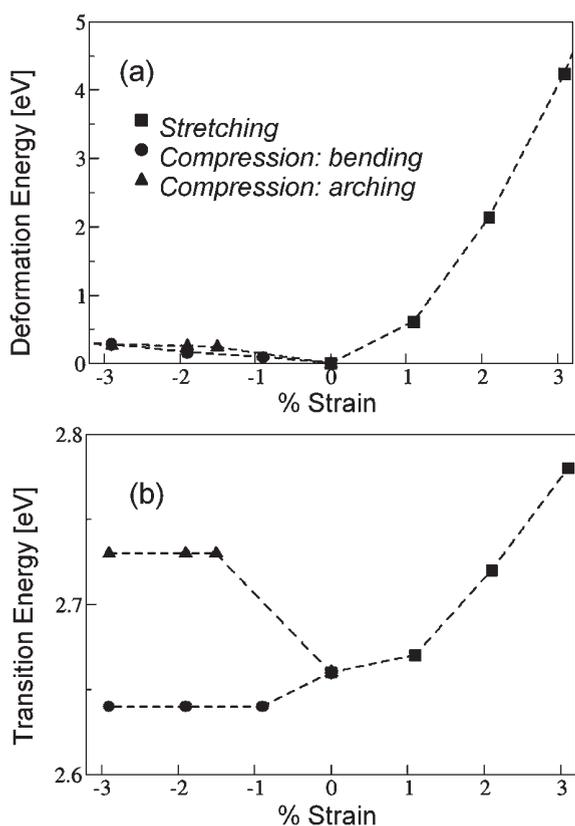
substrate was observed in these calculations, this could potentially occur in general cases of adsorption. We also note that this is unlikely to be a unique adsorption configuration of the polymer on the substrate but demonstrates that the  $\beta$ -phase polyfluorene could chemisorb intact. Specific binding occurs between C atoms in the molecule and the Si dimers. The Si dimers involved in the bonds with the molecule become unbuckled, which corresponds to their configuration on the hydrogenated surface.<sup>25</sup> There is no relaxation of the Si dimers in the direction parallel to the surface plane, and there is no relaxation in subsurface layers. The molecule is extended by 3.6%, and all Si dimers below the molecule are involved in the bonding. The polymer is not adsorbed symmetrically in the axes parallel and perpendicular to the dimer rows and, consequently, is unevenly stretched.

The Wannier centers of electrons situated between the substrate and the molecule shown in Figure 4c demonstrate that covalent bonds are formed between specific C atoms and the Si substrate, and the Wannier orbitals show their distribution over the adsorbate and substrate. The binding between polyfluorene and the Si dimers involves C atoms on opposite sides of the molecule. There is one fluorene unit which is symmetrically bound with a configuration that corresponds to the result of two [4 + 2] cycloaddition reactions. Other than that, the alignment of the molecule with the substrate inhibits symmetrical binding of the monomers. Different C atoms in adjacent six-membered rings are involved in binding, which are not necessarily directly opposite one another in the direction perpendicular to the molecular axis. The C atoms involved in bonding change their hybridization from  $sp^2$  to

**Table 1.** Values of Structural Parameters for Deformed Fluorene Dodecamers Compared to the Undistorted Ground-State Geometry<sup>a</sup>

	undeformed	3% stretch	3% bend	3% arch
C–C between monomers [Å]	1.47	1.52	1.46	1.47
length of monomer [Å]	7.00	7.20	6.98	6.91

<sup>a</sup>The 3% extension results in an increase in both parameters, whereas compression of the molecules by arching or bending does not result in a significant decrease of the linking C–C bond. For bending, the linking bond is decreased in length, whereas the length of the monomer remains the same. In the case of arching, the bond linking monomer units are not compressed, and the reduction in length of the monomer is indicative of arching of the repeat unit itself.



**Figure 3.** (a) The deformation energies associated with morphology changes upon increasing strain. Positive values for strain indicate tensile stretching of the molecule, and negative values indicate compression. The energy associated with stretching increases rapidly beyond 1% strain, whereas there is little change upon compression. (b) The vertical transition energies for the deformed structures in (a). Upon compression, the transition energy can be red- or blue-shifted depending on the change in backbone morphology.

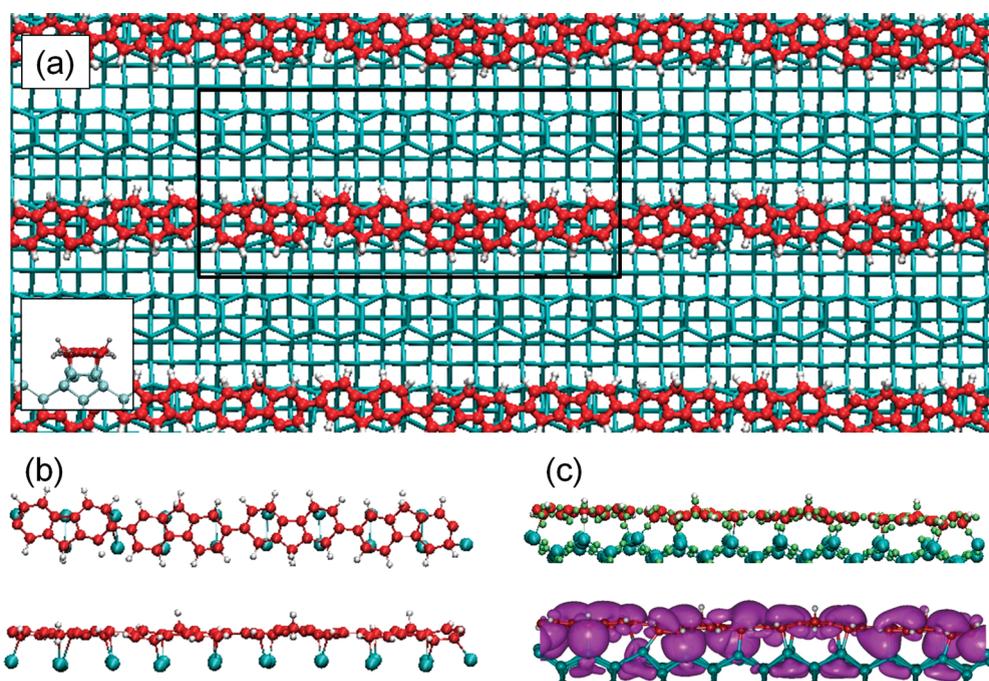
$sp^3$ , which results in buckling of the fluorene monomers, and there are still  $sp^2$  C atoms in the molecule. We note that this bonding configuration is not exclusive for the molecule, with conceivable alternatives depending on the extent of relaxation of the molecule. In our model system, we have enforced elongation of the molecule through a particular alignment with the substrate and found that we obtain a stable bonding

configuration. We find that two of the linking C–C bonds between fluorene monomers are increased to 1.52 Å, but two of the linking bonds are decreased from 1.47 to 1.43 Å. If we consider an isolated fluorene tetramer corresponding to this configuration, part of the molecule is compressed and part extended. The calculated transition energy for this deformed structure is 2.52 eV, which is red-shifted compared to 2.68 eV for the planar fluorene dodecamer, which we take to approximate the polymer. Therefore, although the molecule as a whole is stretched, localized regions in which compression occurs and conjugation is strengthened could potentially dominate its properties.

In conclusion, we have demonstrated that mechanically induced uniaxial strain in a flexible molecular nanowire can affect the vertical transition energy, although shifts are sensitive to potential morphology changes and not just the absolute molecular length. Upon elongation, conjugation along the backbone is weakened as bond lengths increase, with a blue shift of the transition energy as expected. Uniaxial compression, however, results in two distinct but degenerate morphologies. For bending within the molecular plane, compression of bond lengths leads to a red shift in the transition energy, and the loss of planarity upon arching of the molecule blue shifts the transition energy as conjugation is weakened. If we compare this to the experimental results of ref 6, we propose that slight bending could occur within and out of the molecular plane without shifting the frequency from that of the  $\beta$ -phase molecule. The application of uniaxial strain does not influence a single structural parameter but rather is distributed over bond lengths and angles and can also be stored in a molecular shape change.

Upon the adsorption of polyfluorene to a Si(100) substrate, where covalent bonds are formed between the conjugated molecule and the substrate,  $\pi$ -delocalization along the molecular backbone is disrupted. It is, however, possible for polyfluorene to adsorb intact with the molecular axis aligned parallel above the Si dimer rows, demonstrating that this could be a route for inducing uniaxial strain in the molecule. This can result in localized stretching or compression of the molecule, although the molecule is elongated overall, and it is principally the C–C bonds linking fluorene units which are extended or shortened. The shortening of the C–C linking bonds leads to a red shift in the transition energies in isolated structures, corresponding to the adsorption configuration. This potentially entails a greater shift in transition energies than compressing isolated molecules, which accommodate strain by shape change, as interactions between monomers are increased and the nature of the linking bond approaches that of C=C.

The adsorption of conjugated polymers on a Si surface presents an attractive system for the structural manipulation of these flexible molecules. This study demonstrates that manipulation is possible and that the molecule retains its nanowire characteristics with translational symmetry along the backbone, but the principal needs to be developed further if it is to be of practical benefit. Tether substituents could be employed between the substrate and adsorbate to enable the application of directional strain while having a lesser impact on the electronic structure of the molecules. Uniaxial strain in these molecular nanowires, especially if this can be precisely



**Figure 4.** (a) The adsorption configuration of polyfluorene, modeled using four monomer units in a periodically repeating supercell, on the Si(100) substrate. The supercell is indicated in black. The inset gives a view of the adsorbed molecule looking down the Si dimer rows. (b) Close-up views of the adsorption configuration including one Si dimer row; above is a view from the top, and below is a view from the side. The uneven buckling of the polymer can be discerned. (c) The Wannier centers (above), shown by green points, and the Wannier orbitals associated with the centers located between Si and C atoms (below). The centers indicate that there are directional bonds formed between the substrate and adsorbate, and the orbitals indicate a hybridization of molecular  $\pi$ -orbitals with the Si dimers.

controlled, could provide a route for fine-tuning of their optoelectronic properties.

First-principles density functional theory methods<sup>26,27</sup> with the B3LYP exchange-correlation approximation<sup>28,29</sup> and a 6-311g(d) basis set within the Gaussian code<sup>30</sup> were used for the isolated oligomer. Strain is induced by incrementally increasing or decreasing the distance between terminal C atoms in steps ranging between 0.01 and 0.10 Å and allowing all other atomic positions to relax. The vertical transition energies of these distorted structures are then calculated using TDDFT using the same basis set. The adsorption configuration of the fluorenes on a Si(100) slab is determined using the LDA approximation<sup>31</sup> with a plane wave basis set of cutoff 400 eV in the VASP code.<sup>32,33</sup> We use ultrasoft pseudopotentials,<sup>34,35</sup> and the Kohn–Sham wave functions are evaluated at the  $\Gamma$  point of the supercell. We model the substrate with a Si slab consisting of six atomic layers infinitely repeated in the surface plane, and the bottom layer of the slab is hydrogenated. We obtain a clean surface structure consisting of buckled Si dimer rows, in agreement with previous studies.<sup>36</sup> We place polyfluorene 3 Å above the surface, and the molecules are separated from their neighbors by an empty Si dimer row. There is a minimum vacuum spacing of 10 Å between the molecule and the bottom layer of the slab in the direction perpendicular to the surface. The atomic positions of the molecule and top three layers of the substrate are relaxed until a stable adsorption configuration is obtained. The vertical transition energies of the distorted tetramer corresponding to the adsorption configuration are calculated using B3LYP with

a 6-311g(d) basis set, as that for the isolated dodecamers. The Wannier orbitals are calculated using the CPMD code.<sup>37</sup>

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## REFERENCES

- (1) Scherf, U.; List, E. J. W. Semiconducting Polyfluorenes - Towards Reliable Structure–Property Relationships. *Adv. Mater.* **2002**, *14*, 477–487.
- (2) Grell, M.; Bradley, D. D. C.; Ungar, G.; Hill, J.; Whitehead, K. S. Interplay of Physical Structure and Photophysics for a Liquid Crystalline Polyfluorene. *Macromolecules* **1999**, *32*, 5810–5817.
- (3) Chunwachirasiri, W.; Tanto, B.; Huber, D. L.; Winokur, M. J. Chain Conformations and Photoluminescence of Poly(dioctylfluorene). *Phys. Rev. Lett.* **2005**, *94*, 107402.
- (4) Arif, M.; Volz, C.; Guha, S. Chain Morphologies in Semicrystalline Polyfluorene: Evidence from Raman Scattering. *Phys. Rev. Lett.* **2006**, *96*, 025503.

- (5) Becker, K.; Lupton, J. M. Dual Species Emission from Single Polyfluorene Molecules: Signatures of Stress-Induced Planarization of Single Polymer Chains. *J. Am. Chem. Soc.* **2005**, *127*, 7306–7307.
- (6) Da Como, E.; Becker, K.; Feldmann, J.; Lupton, J. M. How Strain Controls Electronic Linewidth in Single Beta-Phase Polyfluorene Nanowires. *Nano Lett.* **2007**, *7*, 2993.
- (7) Hong, S. Y.; Kertesz, M. Theoretical Evaluation of Young's Moduli of Polymers. *Phys. Rev. B* **1990**, *41*, 11368.
- (8) Hong, S. Y.; Kertesz, M. Dependence of Young's Modulus of trans-Polyacetylene upon Charge Transfer. *Phys. Rev. Lett.* **1990**, *64*, 3031.
- (9) Forrest, S. R. Ultrathin Organic Films Grown by Organic Molecular Beam Deposition and Related Techniques. *Chem. Rev.* **1997**, *97*, 1793–1896.
- (10) Kowarik, S.; Gerlach, A.; Schreiber, F. Organic Molecular Beam Deposition: Fundamentals, Growth Dynamics, and in Situ Studies. *J. Phys.: Condens. Matter* **2008**, *20*, 185005.
- (11) Yoshinobu, J. Physical Properties and Chemical Reactivity of the Buckled Dimer on Si(100). *Prog. Surf. Sci.* **2004**, *77*, 37–70.
- (12) Yoshinobu, J.; Tsuda, H.; Onchi, M.; Nishijima, M. The Adsorbed States of Ethylene on Si(100)c(4 × 2), Si(100)(2 × 1), and Vicinal Si(100) 9°: Electron Energy Loss Spectroscopy and Low-Energy Electron Diffraction Studies. *J. Chem. Phys.* **1987**, *87*, 7332–7341.
- (13) Liu, Q.; Hoffmann, R. The Bare and Acetylene Chemisorbed Si(001) Surface, and the Mechanism of Acetylene Chemisorption. *J. Am. Chem. Soc.* **1995**, *117*, 4082–4092.
- (14) Wolkow, R. A. Controlled Molecular Adsorption on Silicon: Laying a Foundation for Molecular Devices. *Annu. Rev. Phys. Chem.* **1999**, *50*, 413–441.
- (15) Tao, F.; Bernasek, S. L.; Xu, G. Q. Electronic and Structural Factors in Modification and Functionalization of Clean and Passivated Semiconductor Surfaces with Aromatic Systems. *Chem. Rev.* **2009**, *109*, 3991–4024.
- (16) Lopinski, G. P.; Moffatt, D. J.; Wolkow, R. A. Benzene/Si(100): Metastable Chemisorption and Binding State Conversion. *Chem. Phys. Lett.* **1998**, *282*, 305–312.
- (17) Lopinski, G. P.; Fortier, T. M.; Moffatt, D. J.; Wolkow, R. A. Multiple Bonding Geometries and Binding State Conversion of Benzene/Si(100). *J. Vac. Sci. Technol., A* **1998**, *16*, 1037–1042.
- (18) Gokhale, S.; Trischberger, P.; Menzel, D.; Widdra, W.; Dröge, H.; Steinrück, H. P.; Birkenheuer, U.; Guddeutsch, U.; Rösch, N. Electronic Structure of Benzene Adsorbed on Single-Domain Si(001)-(2 × 1): A Combined Experimental and Theoretical Study. *J. Chem. Phys.* **1998**, *108*, 5554–5564.
- (19) Naydenov, B.; Widdra, W. Vibrational Characterization of Different Benzene Phases on Flat and Vicinal Si(100) Surfaces. *J. Chem. Phys.* **2007**, *127*, 154711.
- (20) Mamatkulov, M.; Stauffer, L.; Minot, C.; Sonnet, Ph. Ab Initio Study of Biphenyl Chemisorption on Si(001): Configurational Stability. *Phys. Rev. B* **2006**, *73*, 035321.
- (21) Cranney, M.; Comtet, G.; Dujardin, G.; Kim, J. W.; Kampen, T. U.; Horn, K.; Mamatkulov, M.; Stauffer, L.; Sonnet, Ph. Electronic Structure of Biphenyl on Si(100). *Phys. Rev. B* **2007**, *76*, 075324.
- (22) Kasaya, M.; Tabata, H.; Kawai, T. Scanning Tunneling Microscopy and Molecular Orbital Calculation of Pentacene Molecules Adsorbed on the Si(100)2 × 1 Surface. *Surf. Sci.* **1998**, *400*, 367–374.
- (23) Weidkamp, K. P.; Hacker, C. A.; Schwartz, M. P.; Cao, X.; Tromp, R. M.; Hamers, R. J. Interfacial Chemistry of Pentacene on Clean and Chemically Modified Silicon (001) Surfaces. *J. Phys. Chem. B* **2003**, *107*, 11142–11148.
- (24) Nunzi, F.; Sgamellotti, A.; Coletti, C.; Re, N. Adsorption and Interfacial Chemistry of Pentacene on the Clean Si(100) Surface: A Density Functional Study. *J. Phys. Chem. C* **2008**, *112*, 6033–6048.
- (25) Rudkevich, E.; Liu, F.; Savage, D. E.; Kuech, T. F.; McCaughan, L.; Lagally, M. G. Hydrogen Induced Si Surface Segregation on Ge-Covered Si(001). *Phys. Rev. Lett.* **1998**, *81*, 3467–3470.
- (26) Hohenberg, P.; Kohn, W. Inhomogeneous Electron Gas. *Phys. Rev. B* **1964**, *136*, B864–B871.
- (27) Kohn, W.; Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev. A* **1965**, *140*, A1133–A1138.
- (28) Becke, A. D. Density-Functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- (29) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle–Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B* **1988**, *37*, 785–789.
- (30) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R. E.; Stratmann, O.; Yazyev, A. J.; Austin, R.; Cammi, C.; Pomelli, J. W.; Ochterski, R.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, revision A.1; Gaussian, Inc.: Wallingford CT, 2009.
- (31) Perdew, J. P.; Zunger, A. Self-Interaction Correction to Density-Functional Approximations for Many-Electron Systems. *Phys. Rev. B* **1981**, *23*, 5048–5079.
- (32) Kresse, G.; Hafner, J. *Ab initio* Molecular Dynamics for Liquid Metals. *Phys. Rev. B* **1993**, *47*, 558–561.
- (33) Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for *Ab Initio* Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B* **1996**, *54*, 11169–11186.
- (34) Vanderbilt, D. Soft Self-Consistent Pseudopotentials in a Generalized Eigenvalue Formalism. *Phys. Rev. B* **1990**, *41*, 7892–7895.
- (35) Kresse, G.; Hafner, J. Norm-Conserving and Ultrasoft Pseudopotentials for First-Row and Transition Elements. *J. Phys.: Condens. Matter* **1994**, *6*, 8245–8257.
- (36) Liu, F.; Lagally, M. G. Interplay of Stress, Structure, and Stoichiometry in Ge-Covered Si(001). *Phys. Rev. Lett.* **1996**, *76*, 3156–3159.
- (37) CPMD; IBM Corp (1990–2008) and MPI für Festkörperforschung: Stuttgart, Germany <http://www.cpmd.org> (1997–2001).