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Electron Transport in a π-Stacking Molecular Chain

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We have investigated the electronic structure and transport properties of a π-stacking molecular chain which is covalently bonded to a H/Si(100) surface, using the first-principles density functional theory approach combined with Green's function method. The highest occupied molecular orbital (HOMO) dispersion is remarkably reduced, but remains noticeable ($\sim$0.1 eV), when a short π-stacking styrene wire is cut from an infinitely long wire and sandwiched between metal electrodes. We find that the styrene chain's HOMO and lowest unoccupied molecular orbital (LUMO) states are not separated from Si, indicating that it does not work as a wire. By substituting $-NO_2$ or $-NH_2$ for the top $-H$ of styrene, we are able to shift the position of the HOMO and LUMO with respect to the Fermi level. More importantly, we find that the HOMO of styrene$-NH_2$ falls into the band gap of the substrate and is localized in the π-stacking chain, which is what we need for a wire to be electrically separated from the substrate. The conductance of such an assembly is comparable to that of Au/benzene dithiolate/Au wire based on chemical bonding, and its tunability makes it a promising system for a molecular device.

I. Introduction

The demonstration by Wolkow and colleagues[1] that co-valently bonded organic molecular chains can be grown on a hydrogen-terminated silicon surface in a self-directed manner has been making molecular electronics more promising and exciting. Through such design, the geometric uncertainty suffered by molecular wire junctions made of metal-electrode/molecule contacts, partly due to metal diffusion and/or bridging over molecules, can be completely avoided when the device is built on a semiconductor and the interface structure determined by covalent bonding.[2] In addition to styrene,[3,4] other molecular chains derived from molecules such as vinylferrocene,[5] allylm-ercaptan,[6] and aldenhydes[7] have also been successfully grown on the H/Si(100)-2×1 surface. Investigations on the electron transport through the Si(100)-based single styrene molecule have uncovered some intriguing properties. Using ultrahigh vacuum scanning tunneling microscopy (STM) and spectroscopy (STS), Guisinger et al. observed and measured the room-temperature negative differential resistance (NDR) through an individual styrene molecule.[8] A recent breakthrough in how to regulate the electron transport in a single molecule is achieved by Wolkow's group, through changing the charge state of a silicon surface atom in the vicinity of that molecule.[9] Experimental efforts notwithstanding, the measurement of the flow of charges through the π-stacking molecular chain still represents a challenge mostly due to the difficulty of establishing electrodes at the ends of the chain on the silicon surface.

Theoretically, Rochefort et al. studied the effect of π-orbital coupling on the electronic and electrical properties of a hypothetical one-dimensional stack of benzene dithiolate (BDT)

using tight-binding calculations.[10] It was predicted that the highest occupied molecular orbital (HOMO) and lowest unoc-cupied molecular orbital (LUMO) transmission peaks open up when the intermolecule distance is within 4.0 Å, where the van der Waals interaction is significant, and the conductance at low bias becomes substantial as the intermolecule distance reduces to 3.0 Å. More recently, Liu et al. calculated the conductance of an assumed π-stacking benzene chain terminated by two Au-(111) slabs, by virtue of first-principles density functional theory (DFT) and Green's function methods.[11] They used multilayer rather than monolayer slabs to model the electrodes and optimized both the molecule−molecule and molecule−metal distances, in an effort to simulate a more reallistic device than that treated in ref 10. In addition to the confirmation of what was obtained in the previous work, Liu et al. examined the effect of substituting oxygen-containing groups for one or more hydrogen atoms on the benzene ring. Their numerical results suggest that such a substitution increases significantly both the conductance of the molecular junction at low bias voltage and the molecule−molecule binding energy. Many of the other key issues concerning electron transport in π-stacking molecular chains, nonetheless, remain unaddressed. For instance, a π-stack-ing molecular chain is always supported by a solid surface. What is the effect of the supporter on the flow of charge though the chain? Is the molecular wire being separated from the substrate when acting as an electron conductor? Can we modify the molecules to regulate the electron transmission?

Motivated by these questions, we have carried out a first-principles computational investigation on the electronic structure and conductance of a π-stacking styrene chain grown on a hydrogen-terminated silicon surface. The geometry of the molecular junction we intended to study is sketched in panel a of Figure 1. The silicon surface serves both as a supporter of the wire juction and as the gate electrode if the current flowing through the molecular chain is to be regulated. Notice that since

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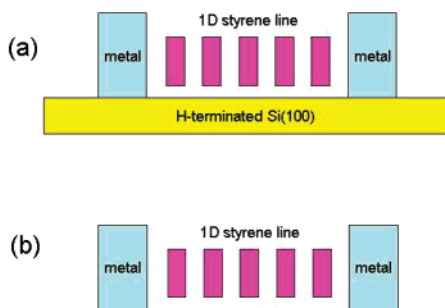‡ National Institute for Materials Science.
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Figure 1. Schematic of a molecular wire junction based on a π-stacking styrene chain with (a) and without (b) the supporting H/Si(100)-2×1 surface.

Figure 2. Calculation model of an infinitely long free-standing styrene chain (a) and an infinitely long styrene (b), styrene$-NH_2$ (c), and styrene$-NO_2$ (d) chain on H/Si(100).

the silicon surface anchors both the molecular chain and the metal electrodes (aluminum) via chemical bonding, the metal/molecule interface structure is quite stable in practice, unlike in the case of molecular wire junctions made only of metal-electrode/molecule contacts. The molecular wire junction depicted in Figure 1a, however, presents a challenge to simulation. The first-principles calculation involving the Si surface is highly demanding due to the large size of the system. On the other hand, the metal/silicon interface has an extremely complicated structure due to both diffusion and lattice mismatch and cannot be readily determined. If the metal electrodes are grown directly on the Si surface, current leakage to the surface will be inevitable, with a magnitude dependent on the particular metal and the interfacial structure of the metal/substrate contact. Or, if we are able to put an insulating buffer between the two, the current leakage can be prevented but the structural and/or electronic perturbations on the electrodes imposed by the buffer (part of the substrate) remain. Computations on this effect are beyond the effort of the current work and deserve a separate set of investigations. As the first step in an attempt to understand how such devices work, we here put the effect of the metal/silicon interface aside and consider metal/molecule and molecule/silicon-surface interactions separately. To evaluate the transmission coefficients, what we dealt with was a simplified device illustrated in Figure 1b instead.

Our calculations show the following: (i) in contrast to the extensively studied case where the organic molecule lies vertically and bonds chemically to the metal electrode,[12] the interaction between the molecular chain and the electrodes in parellel is much weaker than chemical bonding but strong enough to make the HOMO dispersion visible; (ii) the styrene's HOMO and LUMO states are delocalized to have a spatial extension to the Si substrate and does not work as a wire; (iii) by substituting $-NO_2$ or $-NH_2$ for the top $-H$ of styrene, the postions of the HOMO and LUMO can be shifted; (iv) the HOMO of styrene$-NH_2$ falls into the band gap of the substrate and is localized in the π-stacking chain, meaning that the current leak from the styrene chain to the Si substrate is minimal which makes the system a good candidate for a molecular device.

II. Calculation Methods

The density functional theory investigation on the electronic structure was carried out using PHASE.[13] For C, N, and O, the electron/ion interaction was described using ultrasoft pseudo-potentials, and for H and Si, we used norm-conserving ones. We described the exchange correlation between valence electrons using the generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof form.[14] The energy cutoff for the plane wave basis set was 400 eV. The Brillouin zone integration was performed within Monkhorst–Pack scheme
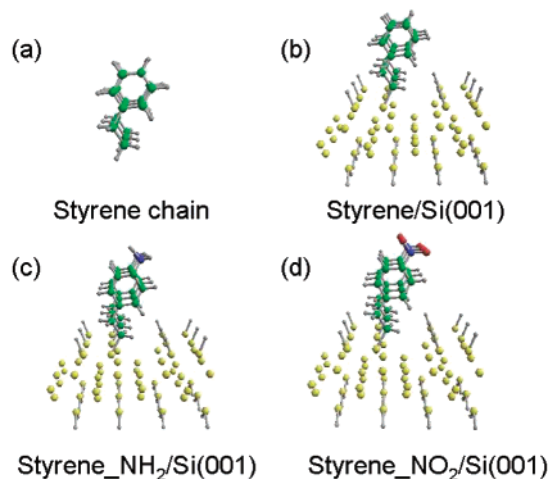
using a $(4 \times 16 \times 1)$ mesh. We model the styrene/Si(100) surface with periodic slabs separated by a vacuum region about 10 Å thick. Each slab consists of five Si(100) layers and a chain of styrene molecules, with each bottom Si passivated by two H atoms (Figure 2b). As a reasonable input for the geometry optimization,[15] the initial structure of a styrene chain adsorbed on a H-terminated Si(100)-2×1 surface was adopted from a previous theoretical work by Cho et al.[16] Then, we removed the supporting Si slab and passivated the anchoring carbon atom of styrene with a hydrogen atom at an optimized C$-$H distance. For a junction depicted in Figure 1b, the position of the electrode on each end of the free-standing molecular chain is certainly adjustable. This is not the case in here, however, because both the molecules and the electrodes are assumed to stand on the Si surface. A reasonable setup of the metal$-$molecule separation is 3.86 Å (measured from the metal surface to the anchoring C atom), the same as the molecule$-$molecule distance along the wire, which is also the layer distance in the Si($1\bar{1}0$) direction. The electrode metal was chosen as aluminum, taking only the simplicity of the interface into account. Most metals, including Au,[17] form a complex interface when deposited on a Si surface, whereas Al can be grown epitaxially on Si.[18] To keep the computation affordable, we used a short molecular chain but made sure the interaction between end molecules is negligible.[19]

We calculated the transmission $T(\epsilon)$ of a molecular device using the Green's function approach within DFT.[20–22] In this method, a finite set of local orbitals are employed and the states of the electrodes are treated as those of the bulk material, which is described with the same DFT treatment. For the pseudoatomic orbitals,[23] we used Al6.0-s2p1d1, N4.0-s2p2d2, O4.0-s2p2d2, C4.0-s2p2, and H4.0-s2p2 for the Al, N, O, C, and H, respectively. Al6.0-s2p1d1 means that, for aluminum, the cutoff atomic radius is 6.0 au and two primitive orbitals are used for s and one for p and d orbitals. We adopted the Ceperlry$-$Alder form parametrized by Perdew and Zunger[24] for the exchange-correlation term and the Troullier$-$Martins type for the atomic pseudopotentials.[25] Partial corrections were applied to the pseudopotentials of C, N, and O. The energy cutoff for the real-space mesh is 100 Ry.

The device system is separated into three parts for convenience: semi-infinite left lead (left region), central region, and semi-infinite right lead (right region). The Hamiltonian matrix is therefore given by

$$H = \begin{pmatrix} H_{\mathrm{L}} & H_{\mathrm{LC}} & 0 \\ H_{\mathrm{CL}} & H_{\mathrm{C}} & H_{\mathrm{CR}} \\ 0 & H_{\mathrm{RC}} & H_{\mathrm{R}} \end{pmatrix} \qquad (1)$$

The overlap matrix S is written in the same form as eq 1. The elements of the Hamiltonian and overlap matrices are determined using the OpenMX code[23] based on the DFT. Green's function $G(z)$ is defined as $G(z) = (zS - H)^{-1}$, where $z = \epsilon \pm i\eta$, with η being an appropriately small real number. Then, the Green function at the central region, $G_{\mathrm{C}}(z)$, can be calculated in the following way

$$G_{\mathrm{C}}(z) = [zS_{\mathrm{C}} - H_{\mathrm{C}} - \sum\nolimits_{\mathrm{L}}(z) - \sum\nolimits_{\mathrm{R}}(z)]^{-1}$$

$$\sum\nolimits_{\mathrm{L}}(z) = (zS_{\mathrm{CL}} - H_{\mathrm{CL}})G_{\mathrm{L}}(z)(zS_{\mathrm{LC}} - H_{\mathrm{LC}}) \qquad (2)$$

$$\sum\nolimits_{\mathrm{R}}(z) = (zS_{\mathrm{CR}} - H_{\mathrm{CR}})G_{\mathrm{R}}(z)(zS_{\mathrm{RC}} - H_{\mathrm{RC}})$$

in which $G_{\mathrm{L/R}}(z) = (zS_{\mathrm{L/R}} - H_{\mathrm{L/R}})^{-1}$ is the surface Green function for the left and right regions. The matrix elements for the layers neighboring the central region[26] are also calculated. The transmission $T(\epsilon)$ is then evaluated as

$$T(\epsilon) = 4Tr\left[\mathrm{Im}\left\{\sum\nolimits_{\mathrm{L}}^{\mathrm{r}}(\epsilon)\right\}G_{\mathrm{C}}^{\mathrm{r}}(\epsilon)\mathrm{Im}\left\{\sum\nolimits_{\mathrm{R}}^{\mathrm{r}}(\epsilon)\right\}G_{\mathrm{C}}^{\mathrm{a}}(\epsilon)\right] \qquad (3)$$

with $G_{\mathrm{C}}^{\mathrm{r}}(\epsilon)(G_{\mathrm{C}}^{\mathrm{a}}(\epsilon))$ and $\sum\nolimits_{\mathrm{L/R}}^{\mathrm{r}}(\epsilon)$ denoting the retarded (advanced) Green function for the central region and the retarded self-energy of the left and right regions, respectively.

III. Electronic Structures

The atomic structures of a free-standing styrene molecular chain and one grown on a Si surface with or without chemical modification are shown in Figure 2. As mentioned in section II, the initial structure of a styrene chain adsorbed on a H-terminated Si(100)-2×1 surface was adopted from a previous theoretical work by Cho et al.[16] Since we used the same density functional as in ref 16, we obtained the same optimized structure as expected. For an isolated styrene molecule, the HOMO$-$LUMO gap calculated with PHASE is 4.8 eV by PHASE, which compares well with the measurement (4.88 eV).[27]

We display in Figure 3 the calculated band structure and local density of states for a free-standing π-stacking styrene chain. To obtain a hypothetical free-standing π-stacking styrene chain, we removed the supporting Si slab and passivated the anchoring carbon atom of styrene with a hydrogen atom at an optimized C$-$H distance. During optimization, the anchoring carbon atom of the styrene molecule was fixed (as in other cases discussed below) to keep the linear structure of the chain. The band dispersion is small for such a weakly bound system, so we plot only a limited number of bands near HOMO and LUMO to better illustrate their dispersion. The bandwidths for the HOMO and LUMO are respectively 0.6 and 0.3 eV, indicating a remarkable molecule/molecule interaction through $\pi-\pi$ coupling. The HOMO$-$LUMO gap is about 4.1 eV, reduced from the isolated molecule by 0.7 eV.

Figure 4 shows us the electronic structure of a styrene chain on H/Si(100). The band gap of the whole system is determined by the silicon supporter. The HOMO of the styrene chain is about 1 eV below the valence band maximum of silicon, whereas the LUMO is 2.5 eV deep into the conduction band of silicon. In view of the fact that the modification of the work function of the metal electrode is not an efficient way to shift the molecular orbitals near the Fermi energy for a metal/
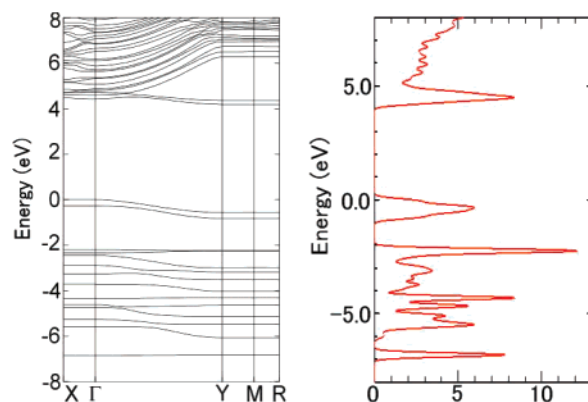

Figure 3. Band structure of an infinitely long free-standing π-stacking styrene chain. The Fermi energy is set to the valence band maximum. See Figure 2b for the geometry.
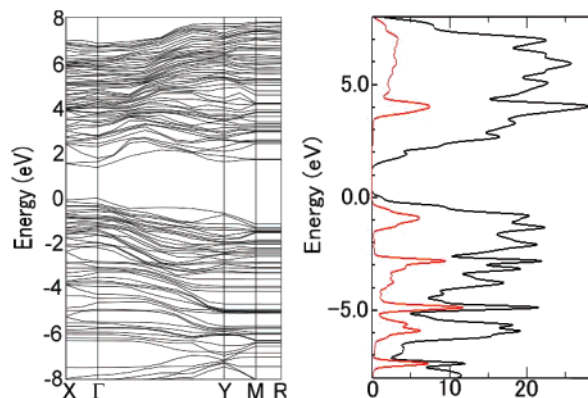

Figure 4. Same as Figure 3 but for an infinitely long free-standing π-stacking styrene chain grown on H/Si(100): (left) band structure; (right) total DOS (black line) and LDOS around the benzene ring (red line). Positions of the HOMO and LUMO are relative to the valence band maximum of silicon. See Figure 2 for the geometry.
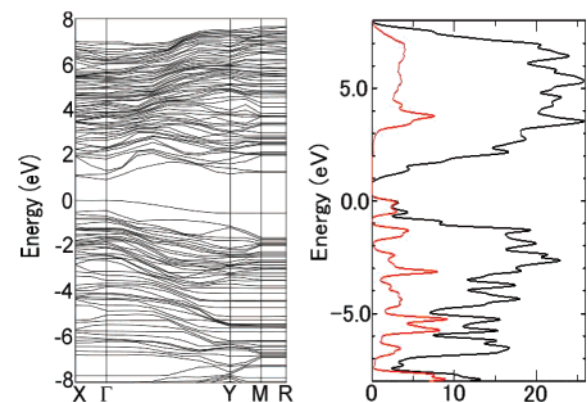

Figure 5. Same as Figure 4, but the styrene molecules are modified to styrene$-$NH$_2$.

molecule/metal contact via chemical bonding,[28] we here modified the styrene molecules by adding side chains such as NH$_2$ (known to act as an electron donating species in many systems) and NO$_2$ in an attempt to explore more efficient molecular conductors.

In Figure 5, we display the electronic structure of a styrene$-$NH$_2$ chain on H/Si(100). We find in this case the band gap of the whole system is no longer determined by the supporting silicon, due to the appearance of the HOMO in the band gap of silicon. NO$_2$, on the other hand, usually acts as an electron accepting species. This is also the case when we modify the styrene molecule with NO$_2$ side chains. It is seen in Figure 6
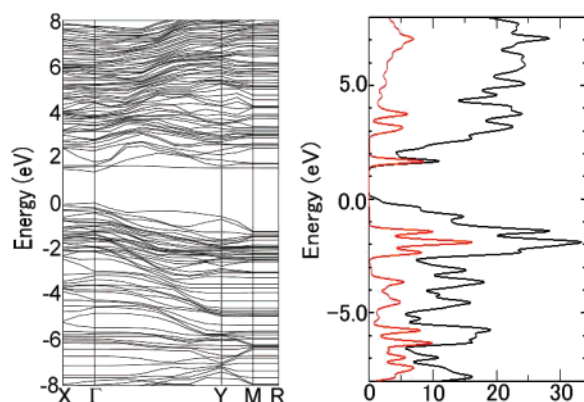
2798 *J. Phys. Chem. B, Vol. 112, No. 10, 2008*

Geng et al.

Figure 6. Same as Figure 4, but the styrene molecules are modified to styrene−NO$_2$.
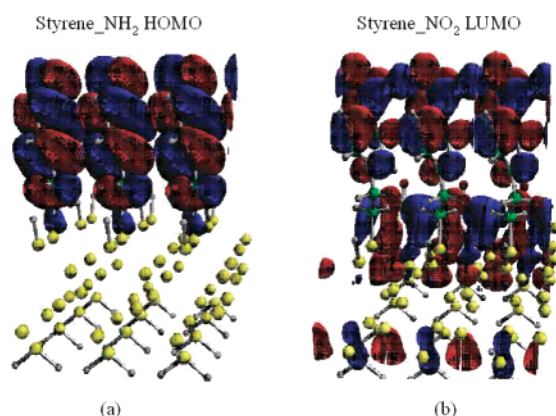

Figure 7. Spatial distribution of the HOMO for styrene−NH$_2$ and the LUMO for styrene−NH$_2$ when they are grown on H/Si(100).
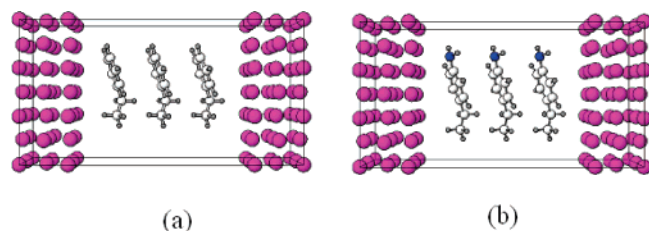

Figure 8. Computation model of (a) Al/3styrene/Al and (b) Al/3styrene−NH$_2$/Al sandwich.

that the LUMO band of styrene−NO$_2$ turns up near the valence band minimum of silicon.

Next, let us see whether the HOMO (LUMO) band of styrene−NH$_2$ (styrene−NO$_2$) will be well separated from the supporting Si substrate when acting as an electron conductor. We plot in Figure 7 the spatial distribution for them. It can be seen clearly that the HOMO of styrene−NH$_2$ is separated from the silicon surface, in accordance with the band structure analysis (see Figure 5), whereas the LUMO of styrene−NO$_2$ has significant distribution on the substrate, as a result of its hybridization with the conduction band of H/Si(100) (see Figure 6). This means that, for the styrene−NH$_2$ grown on H/Si(100), the silicon surface acts only as a supporter of the wire but not a current divider. This is exactly what we require for a molecular chain to serve as an electrical device.

We then attached a three-layer Al(100) slab truncated from the bulk Al to each end of a three-molecule chain at a distance of 3.86 Å, the same as the lattice constant of this 1D structure (see Figure 8 for a unit cell). The lattice constant of bulk Al was 4.06 Å from our GGA calculation. Perpendicular to the

chain, an 8.12 Å × 12.18 Å two-dimensional cell, i.e., Al(100)−2 × 3, was adopted.

In this assembly, the binding energy between the styrene chain and the Al electrodes, defined as the energy release when a short chain consisting of three styrene molecules is inserted into the space between the electrodes, is calculated to be 0.41 eV within GGA. To have more detailed knowledge about the Al/styrene interaction, we varied the electrode−molecule distance and traced the total energy change. We find that the device has the lowest total energy at an electrode−molecule separation of about 4.85 Å, with an energy about 0.55 eV lower than what we set for that based on Si(100). This result *seemingly* indicates a compression of the molecular chain between Al electrodes. Since the conventional local density approximation and the like is not a good description of the long-range dispersion interactions for molecule−molecule and metal−molecule systems,[29] any interpretation should be made with great care. While the GGA usually underestimates the strength of van der Waals-like interactions, the LDA tends to overestimate it. Thus, the above binding energy yielded by GGA can be viewed as the minimum of the real interaction. The binding energy of the −NH$_2$ derivatives to the electrodes is 0.53 eV, about 30% higher than that of the styrene chain (0.41 eV), suggesting an increased molecule−metal binding which is welcomed for the purpose of electron transport through the device.

Moreover, since the detailed Al(001)/Si(100) interface structure is unknown, there is an arbitrariness in positioning the metal slab in the plane perpendicular to the direction along the molecular line. To illustrate the effect of this uncertainty on metal−molecule binding, we shifted the styrene line in the Al-(010) direction (into the paper in Figure 8) for 2.03 Å. This shift exchanges the on-top and hollow sites with respect to Al-(100) and is expected to exert the most significant effect on the metal/molecule interaction. It turns out that the energy change associated with this shift is only 0.02 eV, about 5% of the metal−molecule binding energy.

IV. Transport Properties

Using the Green's function method, we have calculated the transmission coefficients for a hypothetical molecular device illustrated in Figure 8. Limited by the computational cost we can afford, we want to model a molecular junction composing only a short piece of styrene chain, but not so short as to make the end molecules interacting with each other. As mentioned above, we have calculated the binding energy for a short isolated styrene chain composed of two to five molecules and found that a three-molecule chain is long enough to minimize the interaction between end styrene molecules (<0.01 eV).[19]

To examine how the transmission is influenced by chemical modification of the molecules, we studied chains composed of styrene−NH$_2$ or styrene−NO$_2$. Figure 9 displays the calculated electron transmission $T(\epsilon)$ (gray curves) through a short π-stacking styrene chain consisting of three styrene molecules sandwiched between Al electrodes at zero bias voltage. Also shown is the projected density of states (PDOS) with respect to the molecular orbitals from HOMO-2 to LUMO+1 localized at the left, center, and right molecules.

The most striking feature shown in Figure 9 is that the transmission curves match extremely well the PDOS at the center molecule, but not those of the left and right molecules. The excellent match of transmission curves and PDOS curves
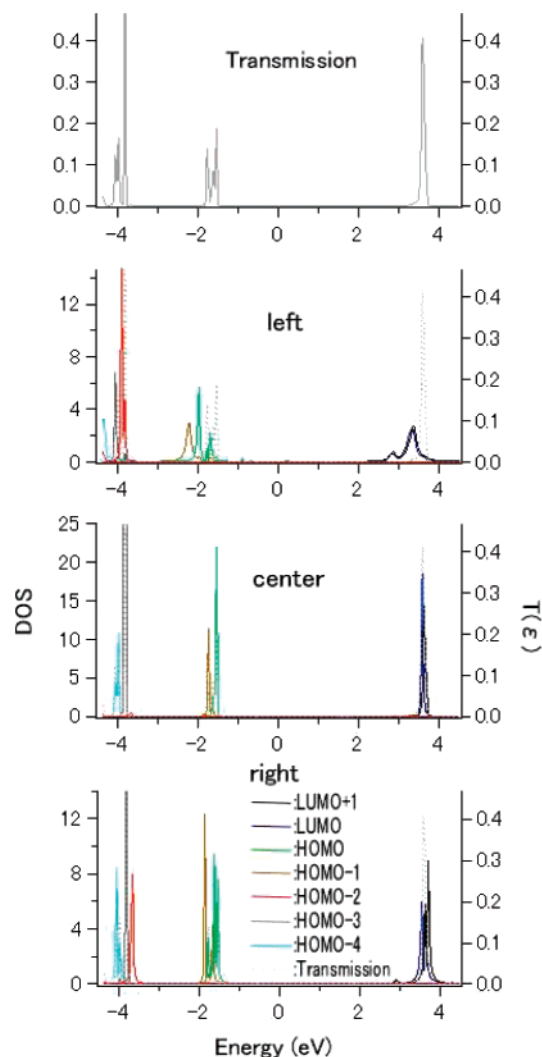
Electron Transport in a π-Stacking Molecular Chain

J. Phys. Chem. B, Vol. 112, No. 10, 2008 **2799**

Figure 9. The transmission for an Al/styrene-wire/Al junction at zero bias voltage and the projected density of states (PDOS) with respect to the molecular orbitals from HOMO-1 to LUMO+1 localized at each molecule.

is analogous to the case of a molecular junction based on covalent molecule−metal bonding (Au/benzene dithiolate/Au).[30,31] We can therefore readily attribute each transmission peak to its corresponding molecular orbital(s). Since the PDOS of the molecule has a vanishing value at the Fermi level, the calculated conductance at the Fermi level is also very low, only about $4 \times 10^{-7} G_0$. It is interesting to note that the PDOS at the end molecules are quite different from those at the center of the π-stacking chain (center molecule). This is the consequence of the styrene/Al interaction, which results in some hybridized states around each molecular orbital. Due to the different interface geometry at the two electrodes, the PDOS at the left and right ends of the chain are also different. These results indicate that the end molecules of the chain act like parts of the electrodes that are only weakly bound to the molecular chain.

Since the molecule/electrode interaction is not of covalent type, great modification of the PDOS with respect to the molecular orbitals can only be realized by chemical modification of the component molecules. As we have demonstrated in section III, a replacement of the top H of styrene with NH_2 will shift the molecular orbitals closer to the Fermi energy. Also, more interestingly, the charge distribution of the HOMO of styrene−NH_2 is separated from the silicon surface, which is ideal for a molecular chain to serve as an electrical device. We
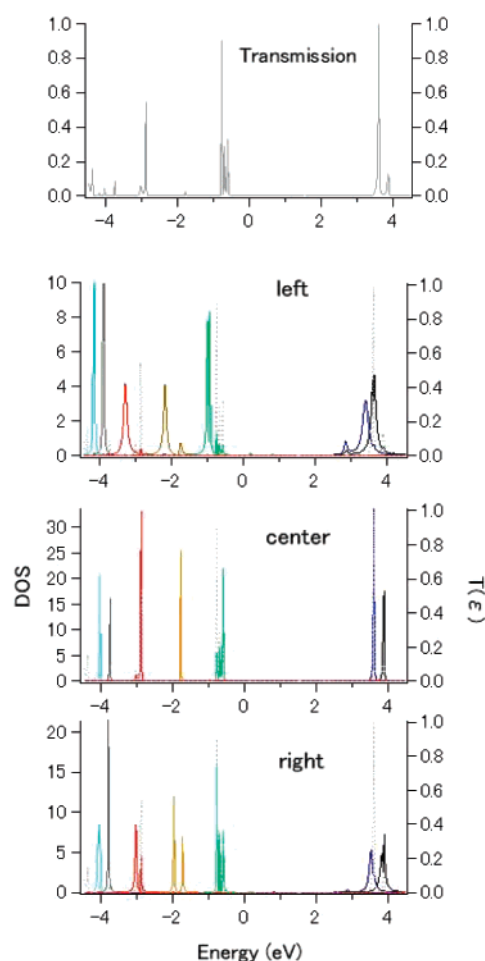

Figure 10. Same as Figure 9 but for styrene−NH_2.

see in Figure 10 that the HOMO−LUMO gap is reduced by 1.0 eV upon such a chemical modification, and the resonant transmission induced by the HOMO shifts 1 eV to the Fermi energy. The conductance at the Fermi level, nevertheless, is hardly changed and remains as small as $1 \times 10^{-4} G_0$. The current flow through the molecular wire in an energy window [−1.2 eV, 0.3 eV] is 1.56 μA, comparable to that through a Au/benzene dithiolate/Au wire based on chemical bonding (1.5 μA for a bias voltage of 0.5 V).[32] Notice that we evaluate the current simply by integrating the zero bias transmission profile in the energy window considered. This is not an exact approach because the whole transmission profile is bias-dependent. Therefore, an out-of-equilibrium approach is necessary if one has to compute the current precisely. Our estimation of current, however, is expected to be valid at least for the order of magnitude. Since Al can be grown epitaxially on Si,[18] it might be possible for experimentalists to build up nanoscale Al electrodes at the end of the π-stacking molecular chain on H/Si-(100). If an assembly such as Al/styrene−NH_2/Al on H/Si(100) can be realized, the current flowing through the wire at low bias will be significant enough to detect. To testify our computational result, experimental work is necessary.

To end the discussion, we want to give an explanation on the choice of exchange-correlation forms. We did not intend to use different functionals for electronic structure and transport calculations. Both PHASE (for electronic structure calculation) and ASCOT (for transport calculation) are newly developed codes. At the present time, we have implemented only GGA in the PHASE code and only LDA in the ASCOT. Coding work involving implementation of more functionals into these two

simulation packages is in progress. For solid insulators, the valence-conduction band gap, the cohesive energy, and many other properties, given by first-principles calculations, are well-known to vary strongly with the functional used for describing the exchange-correlation interactions; for many sorts of molecules, the HOMO−LUMO gap is also quite dependent on the exchange-correlation functional being used. To figure out the scale of this variation for a styrene molecule and a styrene chain, we have carried out computations using the Vienna Ab initio Simulation Package (VASP)[32] on the HOMO−LUMO gap. We find that, for an isolated styrene molecule, LDA (ref 24) gives a gap of 4.82 eV and GGA (ref 14) gives 4.80 eV, very similar to each other. For an infinitely long free-standing styrene chain, we first varied the intermolecular distance to calculate the binding energy. With LDA, it is 0.21 eV per molecule; with GGA, the number is 0.02 eV. We note that the latter value is around the numerical error. As expected, LDA gives a pretty strong cohesion of π-stacking molecules; GGA, on the other hand, predicts an extremely weak binding, if not at all. The HOMO−LUMO gap, however, is very insensitive to the choice of exchange-correlation functional (LDA, 4.20 eV; GGA, 4.18 eV), similar the isolated molecule case. With these results, we expect LDA and GGA to predict a similar HOMO−LUMO gap for the Al/styrene/Al assembly.

V. Summary

To summarize, we have first studied the electronic structure of both a free-standing π-stacking molecular chain and one covalently bonded to a H/Si(100) surface, using the first-principles density functional theory approach. Then, we calculated the transmission coefficients of a short chain of free-standing π-stacking molecular wire, with a geometry derived from the chain grown on H/Si(001), using the Green's function method based on the density functional theory. Our numerical results demonstrate unambiguously that the transmission curves match the PDOS extremely well at the center molecule, but not those of the end molecules of the chain. This is a strong indication that the metal electrode, and therefore the molecule/metal interface can only influence the conductance of the wire in an indirect way, i.e., to the extent they can recover the band dispersion for a short chain to that of an infinitely long chain. By substituting −NO$_2$ or −NH$_2$ for the top −H of styrene, we are able to alter the position of the HOMO and LUMO with respect to the Fermi energy, and therefore to adjust the conductance of this device. Significantly, we find that the HOMO of styrene−NH$_2$ falls into the band gap of the substrate and is localized in the π-stacking chain, an indication that there will be no current leak from the styrene chain to the Si substrate. Since in practice such a molecular wire junction always has to be supported by a solid surface, the excellent feature of styrene−NH$_2$ makes the system a good candidate for a molecular device.

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