Non-local Conductance Modulation by Molecules: STM of Substituted Styrene Heterostructures on H-Terminated Si(100)

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One-dimensional organic heterostructures consisting of contiguous lines of CF3- and OCH3-substituted styrene molecules on silicon are studied by scanning tunneling microscopy and ab initio simulation. Dipole fields of OCH3-styrene molecules are found to enhance conduction through molecules near OCH3-styrene/CF3-styrene heterojunctions. Those of CF3-styrene depress transport through the nearby silicon. Thus choice of substituents and their attachment site on host molecules provide a means of differentially tuning molecule and substrate transport at the molecular scale.

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Better understanding and control of molecule-surface interactions are key to furthering advances in catalysis research, thin film deposition and processing, chemical sensing, and molecular electronics. The scanning tunneling microscope remains an invaluable tool for studying molecule-surface interactions at the molecular scale. Its ability to probe electronic structure with sub-Angstrom resolution results from the sensitivity of tunnel current to tip-sample separation and local work function. The first STM reports of molecule-surface interactions were of localized chemical reactions with surfaces [1] [2]. On Si(111), charge distributed within the 7 × 7 unit cell both modulates and responds to reaction with ammonia [3]. On the unpinned n-type GaAs (110) surface, chemisorbed oxygen (being electronegative) images with increased filled-state density from transferred surface charge and induces localized surface band-bending [4]. Imaging microscope remains an invaluable tool for studying molecule-surface interactions at the molecular scale. Its resolution results from the sensitivity of tunnel current to tip-sample separation and local work function. The first STM reports of molecule-surface interactions were of localized chemical reactions with surfaces [1] [2]. On Si(111), charge distributed within the 7 × 7 unit cell both modulates and responds to reaction with ammonia [3]. On the unpinned n-type GaAs (110) surface, chemisorbed oxygen (being electronegative) images with increased filled-state density from transferred surface charge and induces localized surface band-bending [4]. Patterns of surface contrast by NH3 dipole fields on GaAs has also been reported [5]. Spin flip sensitivity of adsorbates to local surface environment [6], and the effect of intermolecular interactions on surface diffusion have been resolved. Underlying two dimensional electron gases, substrate strain and substrate charge transfer have been found to affect adsorbate pair separation.

Observations of discrete intermolecular interactions and their effect on STM imaging contrast are limited. In cryogenic STM work, distance dependent interactions between single Au atoms were studied on NiAl[12]. One dimensional (1D) particle in a box states in Au chains on NiAl[13], and perturbation of these by physisorbed organic molecules have been reported[14, 15]. Studies of charge transfer complexes[16] and coupling between functional groups tethered to molecules are more recent[17]. STM transport in adjacent silicon atoms was found to be perturbed by dipole fields due to molecules located elsewhere in the Si7×7 cell[18], and dipole driven ferroelectric assembly of styrene at 7K has been reported [19].

We present experimental (300 K) and theoretical results that show dipole fields produced by substituents bound to aromatic rings on styrene molecules significantly perturb transport characteristics of the host molecules, nearby molecules, and the substrate to which the molecules are attached. For one-dimensional para-substituted OCH3-styrene/CF3-styrene molecular heterostructures, transport through molecules at the heterojunction deviates from that of molecules elsewhere within the structure. In the case of lines of CF3-styrene arranged side by side, the dipole fields increase the ionization potential of underlying silicon valence electrons.

Organic molecular heterostructures were grown using a vacuum phase self-directed growth mechanism[20] for styrene on H-terminated Si(100) 2 × 1 surfaces[22]. Dangling bonds on the H:Si(100) surface initiate a chain reaction between surface Si atoms and styrene, leading to well ordered 1D molecular arrays along Si dimer rows. Heterostructures were formed by first dosing CF3 (electron withdrawing) and then OCH3 (electron donating) para-substituted styrene molecules. Such substituents are of interest as they modify the energy and spatial distribution of π and π* states in host aromatic molecules.

Fig.1 shows the growth and bias-dependent STM imaging of two CF3-styrene/OCH3-styrene heterowires on H:silicon. Fig.1(a) shows a 16nm×26nm region of the sample after a 10L (1L = 10^-6 Torr sec) exposure of CF3-styrene. Sample bias Vs was -3.0V. Arrows label the reactive dangling bonds at the ends of two CF3-styrene segments where their growth terminated. Due to slight tip asymmetry, CF3-styrene bound to either side of their host dimers image with slightly different corrugation. Comparison with images of the unreacted H:Si surface (not shown) shows the upper (lower) CF3-styrene segments are chemically bound to the right (left) sides of their respective dimer rows. Fig.1(b) shows the same region (Vs=-3.0V) following a subsequent 10L exposure of OCH3-styrene. Lines of OCH3-styrene molecules have grown in regions marked by red rectangles, beginning at...
the locations of the terminal dangling bonds of the CF$_3$-styrene lines in Fig.1(a). Thus two CF$_3$-styrene/OCH$_3$-styrene heterowires (‘1’ and ‘2’) have been formed.

At -3.0 V, the tip Fermi-level is below the highest occupied molecular orbitals (HOMO) for the OCH$_3$-styrene since at this bias the tip height at constant current has saturated (see Fig.1(d)). As in our model energy level structure (inset, Fig.1(d)) at high bias the tip Fermi-level (arrow H) is below the highest OCH$_3$-styrene HOMO band (orange) but above the HOMO band of CF$_3$-styrene (violet) which therefore images lower (less bright).

Fig.1(c) shows the same region at $V_s$ = -1.8 V. Here the tip Fermi-level (arrow E, Fig.1(d)) is near the top of the OCH$_3$-styrene HOMO band. The OCH$_3$-styrene continues to image above (brighter than) the CF$_3$-styrene, but the OCH$_3$-styrene molecules near the heterojunctions 1 and 2 now image higher than those further away. The OCH$_3$-styrene in heterowire 1 near the terminal dangling bond also images with increased height.

Fig.1(d) presents topographic cross-sections along heterowire 1 above the trench between its attachment row (labelled with red dots in Fig.1(c)) and the vacant dimer row to its right. The topographic envelope for the heterostructure extends between ~1nm and ~9.5nm along the abscissa. The maxima associated with the terminal dangling bond and the heterojunction are at ~2.3nm and ~6.4nm, respectively. The sloping bias-dependent height response of the OCH$_3$-styrene segment near the terminal dangling bond is much like that reported in Ref. 21 for styrene: On the degenerately doped n-type H:Si surface, dangling bonds behave as acceptors, and carry negative charge. Molecular orbitals belonging to molecules in the vicinity of these charge centres are raised in energy by the localised electrostatic field. Therefore at low filled-state bias, these molecules present increased state density at the tip Fermi-level and image with increased height.

The bias-dependent height response of the OCH$_3$-styrene near the heterojunction is similar to that near the terminal dangling bond just described: At high bias, the interfacial OCH$_3$-styrene images with nearly constant height along the bulk of the homowire segment. As $|V_s|$ decreases, the height of the interfacial OCH$_3$-styrene (4-5 molecules closest to the heterojunction) does not decay as rapidly as in the rest of the OCH$_3$-styrene segment. At $V_s$ = -1.8 V the interfacial OCH$_3$-styrene molecules image ~0.05nm higher than OCH$_3$-styrene situated 5-7 dimers away from the heterojunction 25. This behavior was not expected as there is no dangling bond near the junction.

STM imaging characteristics of related 1D styrene/4-methylstyrene heterostructures on (100) Si were reported in Ref. 26. No height enhancement at the heterojunction was evident in that work. The perturbation due to the methyl substituent gives rise to weaker electric dipoles than those investigated here 27. This suggests that the height enhancement at the CF$_3$-styrene/OCH$_3$-styrene junction may be due to molecular dipoles.
To explore this possibility we carried out \textit{ab initio} density functional calculations \cite{28} of the electrostatic shifts $E_n = -e(W_n - U_n)$ of the local electronic energies where $W_n$ ($U_n$) is the electric potential at the nucleus of atom $n$ in the presence (absence) of all other atoms of the heterostructure. The results for a chain of 10 CF$_3$-styrene and 10 OCH$_3$-styrene molecules on a (100) H:Si cluster are shown in Fig.\ref{fig:2}(a); the relaxed geometry \cite{28} of a part of the heterostructure near the junction is shown at the top of Fig.\ref{fig:2}. The red curve in Fig.\ref{fig:2}(a) shows $E_n$ averaged over the aromatic ring of each molecule where most of the molecular HOMO resides; the OCH$_3$-styrene (CF$_3$-styrene) molecules are to the left (right) of the blue dotted line in Fig.\ref{fig:2}(a). For sterically favored orientations of the OCH$_3$ dipoles (negative O nearer the heterojunction than positive CH$_3$) the red curve rises as the junction is approached from the OCH$_3$-styrene side, peaking at the 2nd OCH$_3$-styrene molecule from the junction. Hence the HOMO level of this molecule is higher in energy than for any other molecule in the chain. Thus for filled state imaging, as the bias voltage $|V|$ increases the STM tip’s Fermi level should cross the HOMO levels of the OCH$_3$-styrene molecules near the heterojunction first, resulting in a pronounced low bias peak in the STM profile of the heterostructure near the heterojunction on its OCH$_3$-styrene side, as is seen experimentally in Fig.\ref{fig:1}(d).

This is supported by detailed transport simulations: Extended Lüttig theory tailored as in Ref. \cite{26} to describe the band structures of Si and tungsten and the electronic structures of molecules, but modified to include the \textit{ab initio} electrostatic energy shifts $E_n$ \cite{28}, was used to model the electronic structure of the system. The STM current was then calculated as in Ref. \cite{26} solving the Lippmann-Schwinger equation to determine the electron transmission probability $T(E,V_s)$ between STM tip and substrate at energy $E$ and bias $V_s$. The Landauer expression $I(V_s) = \frac{2e}{h} \int_{-\infty}^{+\infty} dE T(E,V_s) \left( f(E,\mu_s) - f(E,\mu_d) \right)$, where $f(E,\mu_s)$ and $f(E,\mu_d)$ are the source and drain Fermi functions, was then used to evaluate the current $I$.

Fig.\ref{fig:2}(b) shows the calculated STM current at constant height above the heterowire. Curve C is for a tip Fermi-level $E_F$ just below the highest molecular HOMO state (low STM bias); see the inset, Fig.\ref{fig:1}(d). As discussed above, resonant transmission via this state (centred on the 2nd OCH$_3$-styrene molecule from the junction) results in enhanced current there, consistent with experiment. Curve H shows the calculated current (at higher bias) with the tip Fermi-level below the OCH$_3$-styrene HOMO band; see the inset, Fig.\ref{fig:1}(d). Here resonant tunneling occurs via the HOMO of \textit{every} OCH$_3$-styrene molecule in the array. Thus the relative interfacial current enhancement decreases as absolute current levels rise along the chain, again as in the experiment. These effects result from dipole fields due to OCH$_3$ substituents on the styrene molecules. Simulations with atomic positions unchanged but without electrostatic corrections remove the interfacial current enhancement entirely. Simulations with matrix elements and basis function overlaps responsible for electronic hopping between molecules set to zero did not significantly modify the results reported here. This indicates an electrostatic origin for height enhancement at the heterojunction. Calculations with styrene replacing the CF$_3$-styrene molecules confirm that the interfacial feature is mainly due to OCH$_3$-styrene (rather than CF$_3$-styrene) dipole fields \cite{29}.

Effects of the dipole fields are not limited to molecular energy levels: The black curve in Fig.\ref{fig:2}(a) suggests that the Si valence states may lie $\sim 0.5$ eV lower under the CF$_3$-styrene chain than under the OCH$_3$-styrene. A related heterostructure studied below highlights the response of the underlying silicon to the molecular dipole fields: Fig.\ref{fig:3} shows STM imaging of a triple/single chain of CF$_3$-styrene molecules on H:Si(100). Fig.\ref{fig:3}(a) shows a 15nm×10nm region following a 10L exposure of CF$_3$-styrene ($V_s = -3.0V$). The arrow points to the reactive dangling bond at the end of the longest CF$_3$-styrene line. The ⋆ marks a short double chain of CF$_3$-styrene that has grown beside the long CF$_3$-styrene chain. Figs.\ref{fig:3}(b)-(d) show the same region following a 10L exposure of OCH$_3$-styrene. The end of the long CF$_3$-styrene chain has been extended by $\sim 7$ molecules of OCH$_3$-styrene. Figs.\ref{fig:3}(b)

![Image](image_url)

**FIG. 3:** STM images of a (single-triple CF$_3$-styrene)/OCH$_3$-styrene heterostructure. (a) Short double CF$_3$-styrene line (⋆) beside long single CF$_3$-styrene chain. Arrow marks dangling bond. (b) $V_s = +2V$. Long CF$_3$-styrene chain extended by $\sim 7$ OCH$_3$-styrene molecules. (c) $V_s = -3V$. OCH$_3$-styrene images above CF$_3$-styrene. Single and triple CF$_3$-styrene lines image with similar height. (d) $V_s = -2V$. Single OCH$_3$-styrene and CF$_3$-styrene lines still image above H:Si surface (brighter). Triple CF$_3$-styrene chains image below H:Si surface (black). (e) Constant current topographic cross-sections (0.4nm wide) of CF$_3$-styrene/OCH$_3$-styrene heterowire along trench to right of attachment dimers. Heights are relative to H:Si surface (height = 0nm). Tunnel current: 40pA.
and (c) \( V_s = +2V \) and \(-3V\), image the single and triple CF\(_3\)-styrene segments with comparable height. In Fig.\( 3\)\(d\), \( V_s \) has been reduced to \(-2.0V\) and the region with the triple CF\(_3\)-styrene lines images below (darker than) the single file chain of CF\(_3\)-styrene. Fig.\( 3\)\(e\) shows topographic cross-sections along the CF\(_3\)-styrene/OCH\(_3\)-styrene heterowire. From \( V_s = -3V \) to \( V_s = -2V\), the triple CF\(_3\)-styrene chain (between 7nm and 10nm) images with decreasing height. At \( V_s = -2.0V\), this region images 0.2nm below the H:Si surface indicating depleted silicon state density beneath the molecules at the tip Fermi level.

Transport simulations were undertaken for the related structure shown in Fig.\( 1\)\(a\) (the long CF\(_3\)-styrene line is between the short ones to minimise sensitivity to cluster edges). Fig.\( 1\)\(b\) shows the simulated constant height current along the long CF\(_3\)-styrene line. At low bias (curve \( V \)) current levels drop over the triple CF\(_3\)-styrene qualitatively as in Fig.\( 3\)\(c\): Dipole fields of the CF\(_3\)-styrene lower Si orbital energies below the triple CF\(_3\)-styrene by \( \sim -0.2eV \) more than under the single file CF\(_3\)-styrene. At low bias (\( V_s \sim -2.0V\)) this reduced silicon state density at the tip Fermi level forces the STM tip (in experiment) to move lower over triple CF\(_3\)-styrene than over the H:Si surface to re-establish the fixed tunnel current (40 pA). It can also be concluded in this regime that lateral carrier transfer from the single chain CF\(_3\)-styrene and OCH\(_3\)-styrene regions to the triple chain CF\(_3\)-styrene region is negligible compared with the direct through-molecule transport component.

In summary, we have shown experimentally and theoretically that dipole fields established by strongly electron donating or withdrawing chemical species bound to molecules significantly modulate the transport characteristics of nearby molecules and the underlying substrate. Judicious selection of substituents attached in a site specific manner can be used to tailor electron transport at the molecular length scale and allows differential tuning of molecular vs. substrate transport characteristics.

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\[1\] CIFAR Fellow, Nanoelectronics Program.
\[2\] A.M. Baró, G. Binnig, H. Rohrer, Ch. Gerber, E. Stoll, A. Baratoff, F. Salvan, Phys. Rev. Lett. 52, 1304 (1984).
\[3\] R.A. Wolkow, Annu. Rev. Phys. Chem. 50, 413 (1999).
\[4\] R. Wolkow, Ph. Avouris, Phys. Rev. Lett. 60, 1049 (1988).
\[5\] J.A. Stroscio, R.M. Feenstra, A. P. Fein, Phys. Rev. Lett. 58, 1668 (1987).
\[6\] G. Brown, M. Weimer J. Vac. Sci. Tech. B13,1679(1995).
\[7\] A.J. Heinrich, J.A. Gupta, C.P. Lutz, D.M. Eigler, Science 306, 466 (2004).
\[8\] T. Mitsui, M.K. Rose, E. Fomin, D. F. Ogeltree, M. Salmeron, Phys. Rev. Lett. 94, 036101 (2005).
\[9\] J. Repp, F. Moreasco, G. Meyer, K.-H. Rieder, P. Hyldgaard, M. Persson, Phys. Rev. Lett. 85, 2981 (2000).
\[10\] R. A. Wolkow, Phys. Rev. Lett. 74, 4448 (1995).
\[11\] G.E. Thayer, N.C. Bartelt, V. Ozolins, A.K. Schmid, S. Chiang, R.Q. Huang, Phys. Rev. Lett. 89, 036106 (2002).
\[12\] I. Fernandez-Torrente, S. Monturet, K.J. Franke, J. Fraxedas, N. Lorente, J.I. Pascual, Phys. Rev. Lett. 99, 176103 (2007).
\[13\] N. Nilius, T.M. Wallis, M. Persson, W. Ho, Phys. Rev. Lett. 90, 196103 (2003).
\[14\] T.M. Wallis, N. Nilius, W. Ho, Phys. Rev. Lett. 89, 236802 (2002).
\[15\] N. Nilius, T.M. Wallis, W. Ho, Phys. Rev. Lett. 90, 186102 (2003).
\[16\] G.V. Nazin, X. H. Qiu, W. Ho, Science 302, 77 (2003).
\[17\] F. Jäckel, U.G.E. Perera, V. Iancu, K.-F.Braun, N.Koch, J.P.Rabe, S.-W.Hla, Phys.Rev.Lett. 100, 126102 (2008).
\[18\] P.A. Lewis, C.E. Inman, F. Maya, J.M.Tour, J.E. Hutchinson, P.S. Weiss, J. Am. Chem. Soc. 127, 17421 (2005).
\[19\] K.R. Harikumar, J.C. Polanyi, P.A. Sloan, S. Ayissi, W.A. Hofer, J. Am. Chem. Soc. 128, 16791 (2006).
\[20\] A.E. Baber, S.C. Jensen, E.C.H. Sykes, J. Am. Chem. Soc. 129, 6368 (2007).
\[21\] G. P. Lopinski et al., Nature 406, 48 (2000).
\[22\] J. J. Boland, Surf. Sci. 261, 17 (1992).
\[23\] The Si was arsenic-doped with resistivity < 0.005Ω cm.
\[24\] STM imaging was in vacuum < 1x10^-10Torr with W tips.
\[25\] P. G. Piva et al., Nature 435, 658 (2005).
\[26\] Heterowires were studied on multiple H:Si surfaces with different STM tips. Additional images will be presented elsewhere[29].
\[27\] G. Kirczenow et al., Phys. Rev. B 72, 245306, (2005).
\[28\] A. Y. Anagaw et al., J. Phys. Chem. C112, 3750 (2008).
\[29\] Gaussian03 with the B3PW91 functional and LanL2DZ basis was used for electrostatic calculations. Gaussian98 with the UFF model was used to relax geometries.
\[30\] G. Kirczenow, P. G. Piva, R. A. Wolkow, unpublished.